Hypervalent Organobismuth Compounds : Synthesis, Reaction, and Applications to Organic Synthesis(Dissertation_全文)

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学位申請論文

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Hypervalent Organobismuth Compounds:
Synthesis, Reaction, and Applications to Organic Synthesis

（高原子価有機ビスマス化合物の合成、反応及び有機合成への応用）

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General Introduction

Bismuth was already known in the Middle Age and its identity as a specific element was established as early as the middle of eighteenth century. The Clarke number of bismuth 2 X 10^{-5} classifies this element as rare as silver and mercury, but it is not so expensive because large amounts are recovered as a by-product from the refining process of non-ferrous heavy metals. Bismuth has an electron configuration [Xe] $4f^{14}5d^{10}6s^{2}6p^{3}$ and usually utilizes the three 6*p* electrons in bond formation, thus exhibiting the oxidation state +3 in the majority of its compounds. Two 6*s* electrons retained as a lone pair can also be utilized in high oxidation state. The principal uses of bismuth are the manufacture of alloys, medicines, electric devices, catalysts and cosmetics. Low toxicity of this element has led to various bismuth-based preparations administered orally for treatment of intestinal disorders.

However, the usefulness of this element in organic synthesis has been recognized little until the last decade, when extensive works by Barton's, Wada's and our groups revealed the uniqueness and promising potentials of bismuth as the reagent for organic transformations.[1-9] Though the chemistry of organobismuth compounds possessing trivalent or pentavalent bismuth center has been considerably developed in these years, the chemistry of quaternary organobismuth compounds, represented by bismuthane oxides, bismuthane imides, ylides and bismuthonium salts, has remained almost untouched. The main reason why they have been neglected so far may be attributed to the fact that there has been only limited access to these types of compounds. However, some general and more efficient methods for the synthesis of bismuthonium salts and ylides have been developed recently,[10] allowing their chemistry to be explored further.

In this thesis, some novel methods for the synthesis of bismuthane oxides and imides as well as their structures and chemical behaviors have been reported. The author has found that the intramolecular coordinating groups exert great influence on the nature (thermal– and moisture–stabilities and reactivities) and chemistry of bismuthane oxides and imides This thesis provides the best source of information on the chemistry of these type of compounds.

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Chapter 1 Oxidation of Triarylbismuthanes and Stibanes with Iodosylbenzene. Preparation, Reaction and Isolation of Bismuthane Oxides

Abstract

Treatment of triarylbismuthanes **3** with iodosylbenzene under ultrasonic irradiation or gentle heating leads to the generation of triarylbismuthane oxides **2** in good yields, and it was found that their chemical behavior were quite different from those of lighter organopnictogen oxides in the following aspects. Triarylbismuthane oxides **2** are highly reactive against carbon dioxide and water to give triarylbismuth carbonates **6**, and have mild oxidizing ability to convert alcohols, hydrazobenzene and triphenylphosphane into the corresponding carbonyl compounds, azobenzene and phosphane oxide in good yields under completely neutral conditions. The oxides **2** also react with a variety of active methylene compounds to give a variety of products. Attempts to isolate the oxides **2** sometimes gives abnormal products; oxidation of trimesitylbismuthane **3d** and tris-(2-methoxyphenyl)bismuthane **3e** with iodosylbenzene in dichloromethane led to the corresponding trimesitylbismuth dichloride and diarylbismuth chloride, respectively. Triarylbismuthane oxide **23** derived from 10-(4'-methylphenyl)phenothiabismine **22** could be isolated as a stable compound under atmospheric conditions.

Introduction

Oxides of triarylbismuthanes are a class of compounds which have potential as a versatile precursor for a variety of organobismuth(V) compounds.[1] In contrast to the extensive works on lighter organopnicogen oxides, only little attention has hitherto been paid to the chemistry of organobismuthane oxides. The first synthesis of this class of compounds was reported by Goel and Prasad in 1972,[2] who carried out the metathetical reaction of triphenylbismuth dichloride **1a** and silver(I) oxide in a mixture of benzene-water to obtain triphenylbismuthane oxide **2a** as a white polymeric powder in 10~40 % isolated yields. Their oxide **2a** melted at 155 °C, and they supposed that the oxide **2a** exsisted as a polymer, which contained -Bi-O-Bi- linkage, by IR spectrum. They reported a same type of reaction between triphenybismuth dicyanide and mercuric oxide to obtain the oxide **2a**, however, yield and chemical behavior of the oxide were not described.[3] Metathesis reaction between dichloride **1a** and silver(I) oxide resulted in formation of bismuthane **3a** in moist acetone,[4] while triphenylbismuth dihydroxide was formed in water by the same type of reaction.[5]

Triphenylbismuthane oxide **2a** has been tried to prepare by the direct oxidation of bismuthane **3a** with a variety of oxygen transfer reagent to lead discordant results. Attempted oxidation of bismuthane **3a** with hydrogen peroxide,[6] dinitrogen trioxide,[7] potassium permanganate,[8] 1-pyrroline-1-oxide[9] led to none of expected product. And the reaction between the bismuthane **3a** with selenium dioxide gave bismuth selenate and benzeneseleninic acid.[10] Other recent works have not suggested any efficient methods to prepare triarylbismuthane oxides **2**.

Photochemical reduction of uranyl ion[11] or titanium(IV) oxide[12] with bismuthane **3a** have reported to give the oxide **2a**, however, in both reports, there are no information on the chemical nature of the oxide. Conversion of bismuthane **3a** into its oxide **2a** with *N*-bromosuccinimide-hydrochloric acid-potassium bromide system was used for oxidimetric titration of bismuthane.[13] Barton *et al.* reported that the oxide **2a** was unable to cleave *trans*-decaline-9,10-diol, although no method for preparation of the oxide was described.[14] Naumann *et al.* succeeded to prepare the oxide **2a** by the hydrolysis of triphenylbismuthane *N*-(trifluoromethanesulfonyl)imide. Their sample of the oxide **2a** melted at 152-154 °C, which was identical with those of the Goel's sample, though there was no further imformation on spectral feature.[15]

In view of above results, it seems that the chemical nature of organobismuthane oxides remained untached. A similar phenomenon has long been reported for triphenylstibane oxide **4a**, which exists as dimeric or polymeric form.[16] To establish the method for preparation of bismuthane oxides **2**, we carried out the direct oxidation of triarylbismuthanes with a variety of oxidants. Among several oxidants, ozone and iodosylbenzene led to unique and unexpected results. The former oxidized bismuthanes **3** into a mixture of triarylbismuth dicarboxylates at low temperature, and the ratio of the products depended upon the reaction medium.[17] On the other hand, the latter oxidant converted bismuthanes **3** into *soluble* bismuthane oxides **2** effectively under mild conditions. We wish to report herein the novel method of preparation of bismuthane oxides **2**, the mild oxidizing ability of the bismuth oxide function, and the reactivity of them against active methylene compounds.

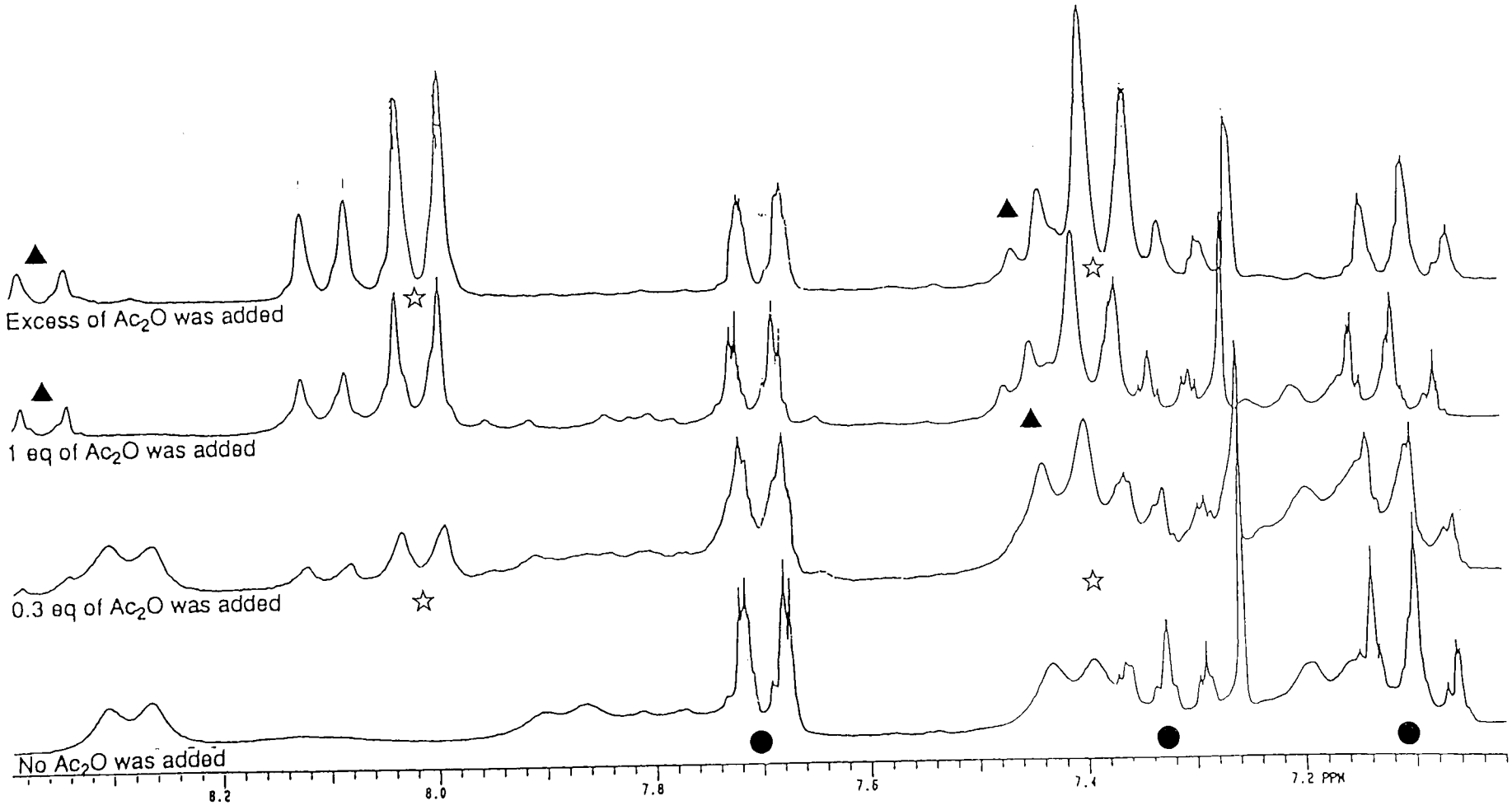
Results and Discussion

In situ Generation of Triarylbismuthane Oxide

First we examined oxidation of bismuthane **3a** with iodosylbenzene in chloroform. The cream yellow starting mixture was stirred at ambient temperature to change into yellow solution after 5 min. The resulting solution was concentrated under reduced pressure to give mixture consisted of iodobenzene, bismuthane **3a** and unidentified compounds. Similar oxidation of tris-(4-methylphenyl)bismuthane **3b** was examined in $CDCl_3$ to get insight of the reaction. The mixture of bismuthane **3b** and iodosylbenzene in $CDCl_3$ was sonicated over ultrasound washing machine for 1 h until it changed into a yellow solution. ^{1}H NMR spectrum of the solution showed broad peaks at around δ 2.37, 7.19, 7.41, 7.84 and 8.28. By the addition of acetic anhydride, these NMR signals were replaced by those of tris-(4-methylphenyl)bismuth diacetate **5b** (for aromatic region, 7.38, d, *J* 8.0 and 8.02, d, *J* 8.0) and tris-(4-methylphenyl)bismuth dichloride **1b** (for aromatic region, δ 7.44, d, *J* 8.0 and 8.36, d, *J* 8.0) (**Fig. 1**).

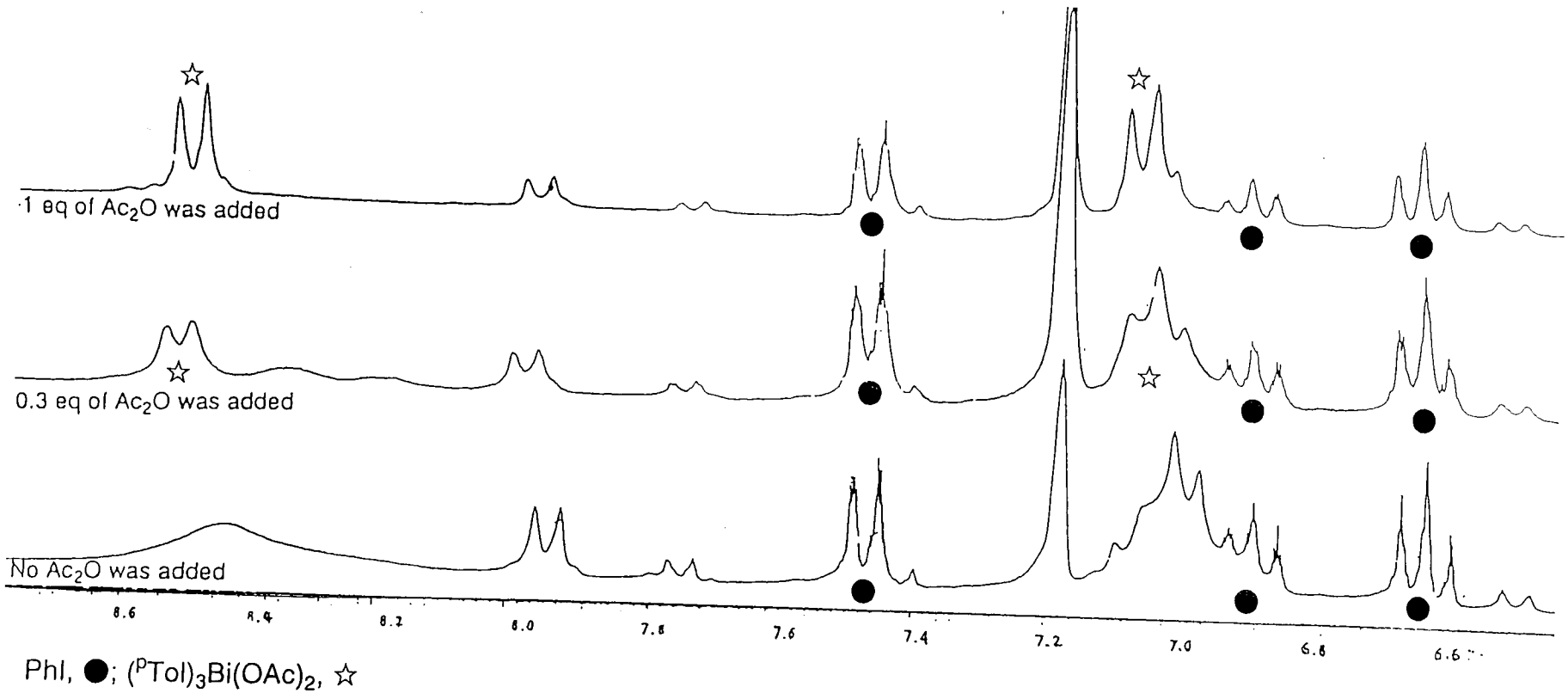
The formation of the latter compound suggested that chloroform reacted with the intermediate of the reaction, and it was less suitable solvent for our purpose. When the sonochemical oxidation of the bismuthane **3a** was carried out in ethyl acetate, triphenylbismuth diacetate **5a** was obtained as the side product, therefor, it was also not suitable solvent. Then the solvent was replaced by toluene or benzene. ^{1}H NMR spectrum (C_6D_6) of a reaction mixture prepared from bismuthane **3b** and iodosylbenzene, exhibited somewhat a broad signal at δ 2.02 and two broad peaks due to

Fig. 1 ^{1}H NMR ($CDCl_3$) spectra of *in situ* generated $^{p}Tol_3Bi{=}O$ **3b**, and its trapping experiment with Ac_2O.

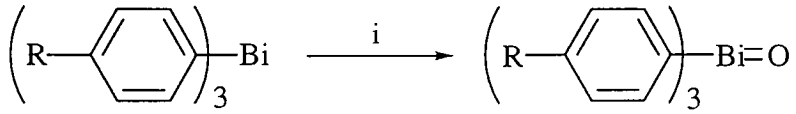


PhI, ●; $(^{p}Tol)_3Bi(OAc)_2$, ☆; $(^{p}Tol)_3BiCl_2$, ▲

Fig. 2 ^{1}H NMR (C_6D_6) spectra of *in situ* generated $^{p}Tol_3Bi{=}O$ **3b**, and its trapping experiment with Ac_2O.



aromatic protons around δ 7.0 and 8.5 with an approximate peak area of 1:1. By the adding of acetic anhydride, these signals were replaced by those of the diacetate **5b** similar to the NMR experiment in $CDCl_3$. A signal at δ 7.98 showed no change during the above procedure (**Fig. 2**). According to the above trapping experiment using acetic anhydride, we may safely conclude that the oxygen transfer reaction from iodosylbenzene to bismuthane occured smoothly, and the bismuthane oxides **2** exist in the yellow solution (**Scheme 1**).



3 **2**

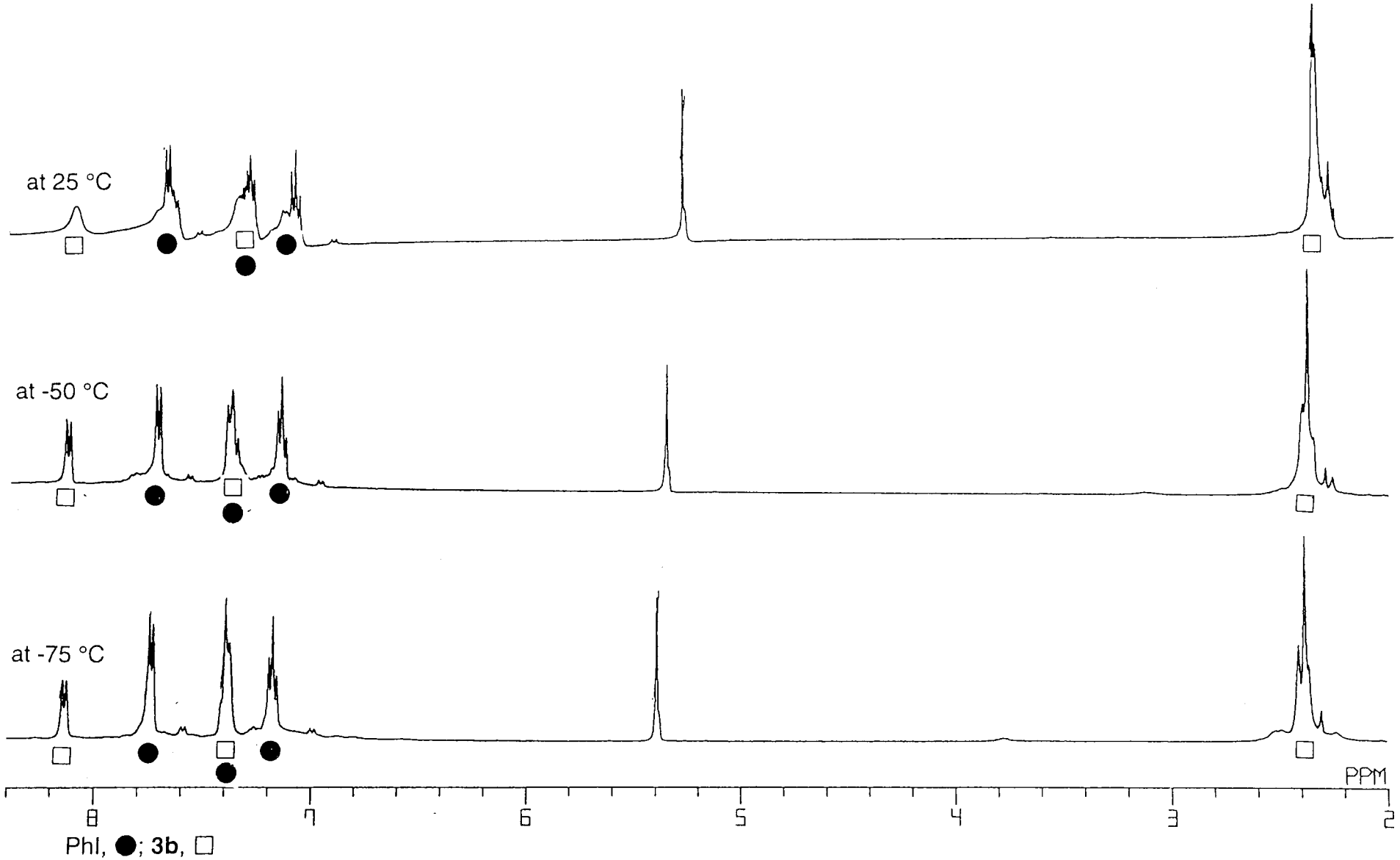
a; R = H, **b**; R = Me, **c**; R =OMe

Scheme 1
Reagent and conditons: i, PhI=O, CH_2Cl_2 or Toluene, 40 °C or)))

After several trial, we have found that dichloromethane is also useful solvent. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of compound **2b** at 25 °C exhibited a methyl signal at δ 2.38 and two broad signals due to aromatic protons at δ 7.4 and 8.2; the latters turned into a pair of doublets (δ 7.39 and 8.14; J = 7.6) below at -50 °C (**Fig. 3**).

The representative procedure for the generation of *soluble* tris(4-methylphenyl)bismuthane oxide **2b** is as follows; tris(4-methylphenyl)bismuthane **3b** (482 mg, 1.0 mmol) was added to a suspension of freshly prepared iodosylbenzene (264 mg, 1.2 mmol) in dry dichloromethane (30 cm^3) and the resulting mixture was sonicated at 35 °C under argon on a commercial ultrasonic washing machine until bismuthane **3b** was completely consumed (checked by TLC).

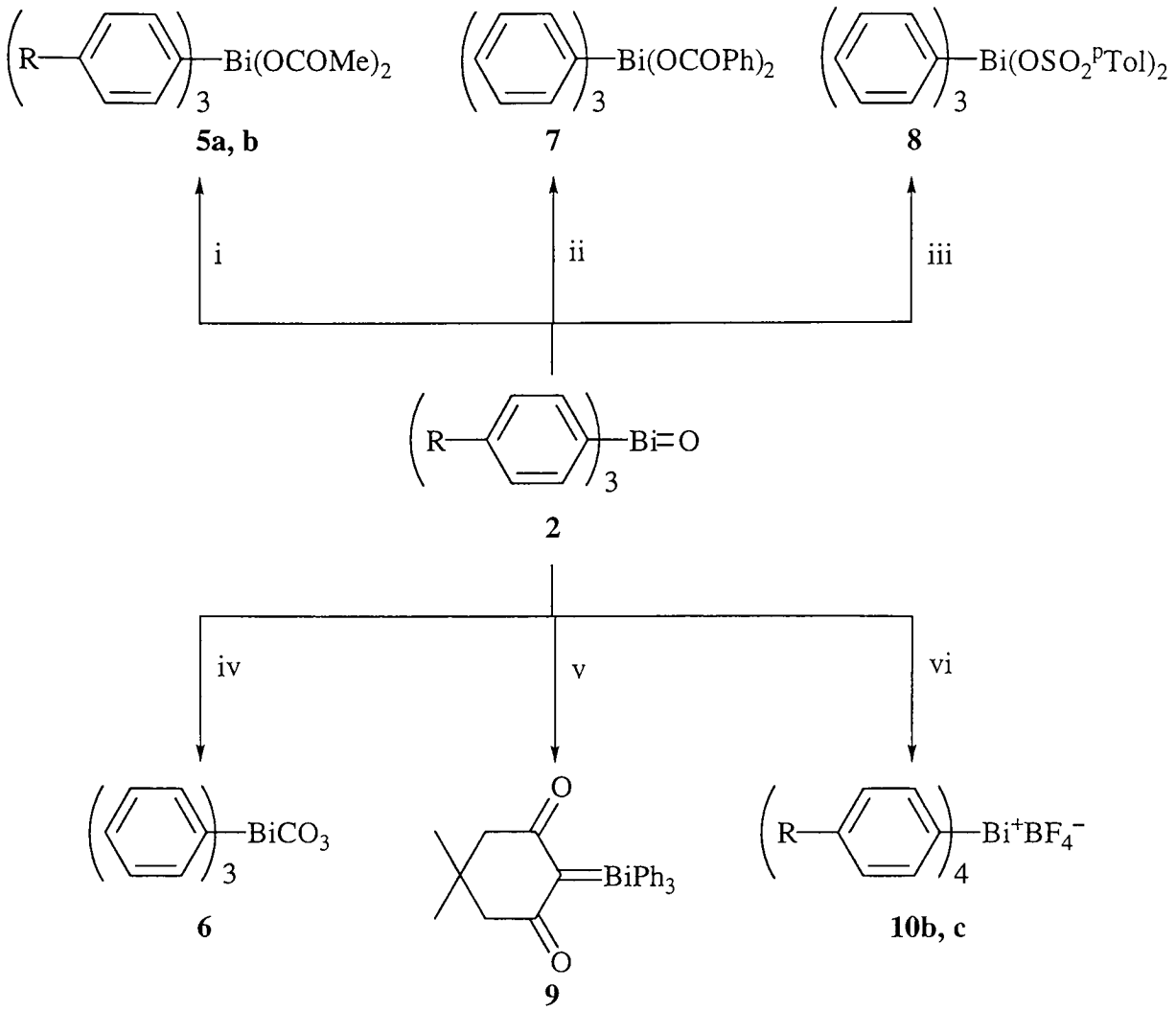
Fig.3 ^{1}H NMR (CD_2Cl_2) spectra of *in situ* generated $^{p}Tol_3Bi{=}O$ **3b** at 25 °C, -50 °C and -75 °C.



After 2~3 h the chalky suspension turned into a bright yellow solution, which was quickly filtered through a Celite bed. When exposed to breath or air, this bright yellow solution gradually lost its characteristic colour, forming triarylbismuth carbonate **6b**[18] as a powdery precipitate. Careful removal of the solvent together with iodobenzene under high vacuum left a glassy residue, which was soluble in benzene, acetone, tetrahydrofuran and dichloromethane, but insoluble in hexane. When scratched by a spatula in hexane, the residue was gradually transformed into an intractable powder, which, however, on stirring for 3 days with a half in weight of triphenylphosphane in benzene at ambient temperature, produced compound **3b** and phosphane oxide in 57 and 65 % yields, respectively, together with unchanged phosphane in 35 % yield. Treatment of a solution of triphenylbismuthane oxide **2a** in toluene with benzoic anhydride or toluene-*p*-sulfonic acid monohydrate afforded triphenylbismuth dibenzoate **7**[19] and bis(toluene-*p*-sulfonate) **8**,[20] respectively, in 66 and 70 % isolated yields (Scheme 2). Reaction between stibane oxides and organosulfonic acids has been reported to give organostibane disulfonates.[20]

Attempts to isolate the presumed oxides **2** by diluting its bright yellow solution with hexane led to a pale yellow precipitate, which was only slightly soluble in benzene. ^{1}H NMR spectrum (C_6D_6) of the precipitation obtained by adding hexane to a solution of bismuthane oxide **2b** agreed with those of the unchanged signals observed in the above mentioned NMR experiment in C_6D_6. Elemental analysis of this precipitate was inconsistent with the theoretical value for compound **2b**. Both the carbon and hydrogen contents were significantly lower than the expected, suggesting the

extensive decomposition of oxide **2b** during the forced precipitation.



Scheme 2

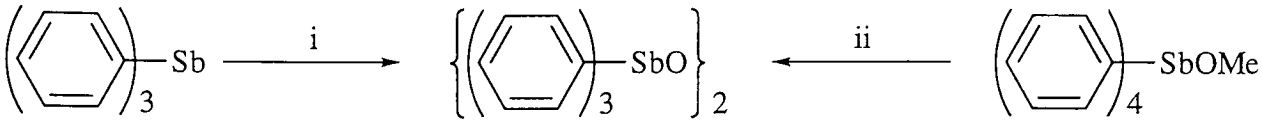
Reagent and conditons: i, $(MeCO)_2O$, r.t.; ii, $(PhCO)_2O$, r.t.; iii, $^pTolSO_3H$, r.t.; iv, CO_2, r.t.; v, dimedone, r.t.; vi, $BF_3 \cdot OEt_2$, -60 °C

In support of this view, its FAB-MS spectrum (*m*-nitrobenzyl alcohol was used as a matrix) contained peaks attributable to fragment ions $PhBi_6O_8$, Bi_6O_8, $Ph_2Bi_5O_6$, Bi_5O_7, $PhBi_4O_5$, $PhBi_3O_3$, Bi_3O_4, Bi_3O_3, $Ph_3BiOCH_2C_6H_4NO_2$, Ph_4Bi, Ph_2Bi, PhBi, Bi and others, suggesting hydrolysis of Bi-C bond caused the formation of these bismuth(III) oxide derivatives. A similar polymeric degradation product was obtained from the autooxidation of trialkylbismuthanes.[21] Reaction of the insoluble solid with 5,5-

dimethylcyclohexane-1,3-dione (dimedone) in dichloromethane under reflux for 2 h led to the formation of a known bismuthonium ylide **9a** in 55% yield.[22,23] Suzuki *et al.* reported the reaction of oxide **2a** with a sodium salt of dimedone to give the ylide **9a**,[24] however, we did not need any additional base for the present reaction. The action of boron trifluoride etherate on compound **2b**,**c** in dichloromethane resulted in the formation of tetraarylbismuthonium tetrafluoroborate **10b** and **10c** in 24% and 6% yield, respectively.

The present sonochemical oxidation procedure was extended to the convenient preparation of triarylstibane oxides; a mixture of triphenylstibane **11a** (353 mg, 1.0 mmol), iodosylbenzene (220 mg, 1.0 mmol) and dry dichloromethane (20 cm^3) was sonicated at ambient temperature for 1 h. Usual workup followed by recrystallization from hexane-dichloromethane (3:1; 20 cm^3) afforded compound **4a** as colourless crystals (310 mg; 84%), mp 219-221 °C (lit.[16] 220-222 °C). Crystalline stibane oxide **4a** has previously been prepared by the thermal decomposition of methoxytetraphenylantimony **12**; heating of this compound at 60-70 °C in xylene for 6 days gave the oxide **4a** in 31% yield (Scheme 3).[16] Direct oxidation of stibane **11a** with hydrogen peroxide produced polymeric stibane oxide as an amorphous solid.[16] In contrast to triphenylphosphane oxide and triphenylarsane oxide which occur in monomeric form, the crystalline form of compound **4a** has been shown by X-ray analysis to exist in a dimeric state.[16] Little information for ^1H NMR spectrum of the stibane oxide is available; McEven had reported that ^1H NMR spectrum (CCl_4) of triphenylstibane oxide exhibited two regions with centre at δ 7.28 and 7.58.[25] ^1H NMR spectrum ($CDCl_3$) of the oxide **4a** which prepared by sonochemical oxidation exhibited two

regions with centre at δ 7.35 and 7.74.



11a **4a** **12**

Scheme 3
Reagent and conditons: i, PhI=O, CH_2Cl_2,))); ii, Xylene, heat

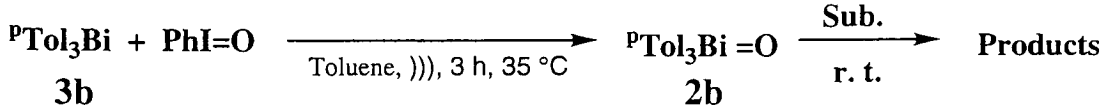
Judging from the above results, it seems that the bismuthane oxides are air and moisture sensitive. This indicates that the previous method would be less suitable for the preparation of the oxides. In fact, metathesis reaction between dichloride **1b** and silver(I) oxide led to the formation of bismuthane **3b** and unidentified compound. ^{1}H NMR signals due to the latter product agreed with those of observed in direct oxidation of bismuthane **3b** in PhI=O–$CDCl_3$ system. Attempt to isolate the product failed due to its instability, although spectroscopic data suggested the structure as μ-oxybis-(4-methylphenyl)bismuth dichloride.[2]

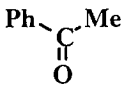
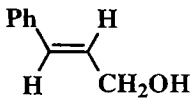
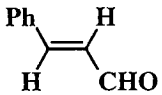
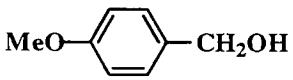
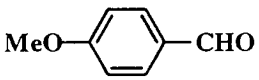
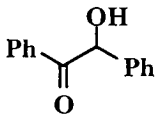
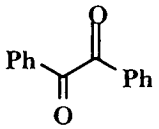
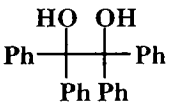
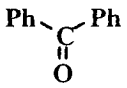
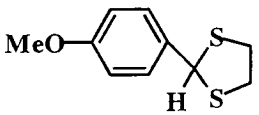
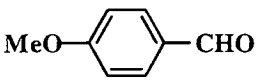
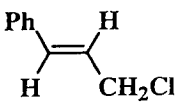
Reactivity of Triarylbismuthane Oxides

The *soluble* triarylbismuthane oxides **2** proved themselves to be a mild oxidizing agent for some organic compounds under neutral conditions (**Table 1**). They easily converted secondary alcohols to ketones, allylic and benzylic alcohols to aldehydes, benzoin to benzil, and benzopinacol to benzophenone. Similar oxidation reaction using bismuth carbonates **6** under basic condition was reported by Barton and co-workers.[26] Hydrazobenzene was rapidly dehydrogenated to azobenzene, and triphenylphosphane was oxidized to phosphane oxide. Organic sulfides such as thioanisole and methyl *n*-octyl sulfide remained intact even after

stirring for 6 days at ambient temperature. In the presence of an equimolar boron trifluoride etherate, 2-(4-methoxyphenyl)-1,3-dithiolane was cleaved to form 4-methoxybenzaldehyde in 33% yield. Cinnamyl chloride remained unchanged after treatment with a solution of the bismuthane oxide **2b**. No obvious improvement was observed by the addition of tetra-(*n*-butyl)ammonium bromide to the reaction mixture. Based on these results, we have concluded that the bismuthane oxides have poor nucleophilicity in contrast that amine *N*-oxides react as nucleophiles.[27] These results might support the hypothesis that bismuthane oxides exist in oligomelic form consist of -Bi(Ar)3-O- repeating unit so that the oxygen has only poor nucleophilicity. In contrast, stibane oxide **4a** has been found to exhibit only a limited ability as oxidant for organic substrates; stirring of an equimolar mixture of stibane oxide **4a** and a given substrate in dichloromethane at ambient temperature under argon resulted in most cases in the recovery of starting materials. Exceptions are benzoin and benzopinacol, which were oxidized to benzil and benzophenone, respectively. Baechler claimed that stibane oxides is less reactive as an oxygen donor against phosphane than triphenylarsane oxide.[28] By addition of $CDCl_3$ solution of bis(*tert*-butyldimethylsilyl) selenide to a C_6D_6 solution of oxide **2b**, and the change of the NMR signals was observed. The formation of bismuthane **3a** would support the oxygen transfer from bismuth to silicon readily underwent in contrast to the inertness of both amine *N*-oxides and phosphine oxides against disilylcharcogenides.[29] These results clearly show the different chemical nature of the "Bi=O" compared with the other pnicogen oxide P=O, As=O and Sb=O.

Table 1. Oxidation of Organic substartes with Bismuthane Oxide **2b**

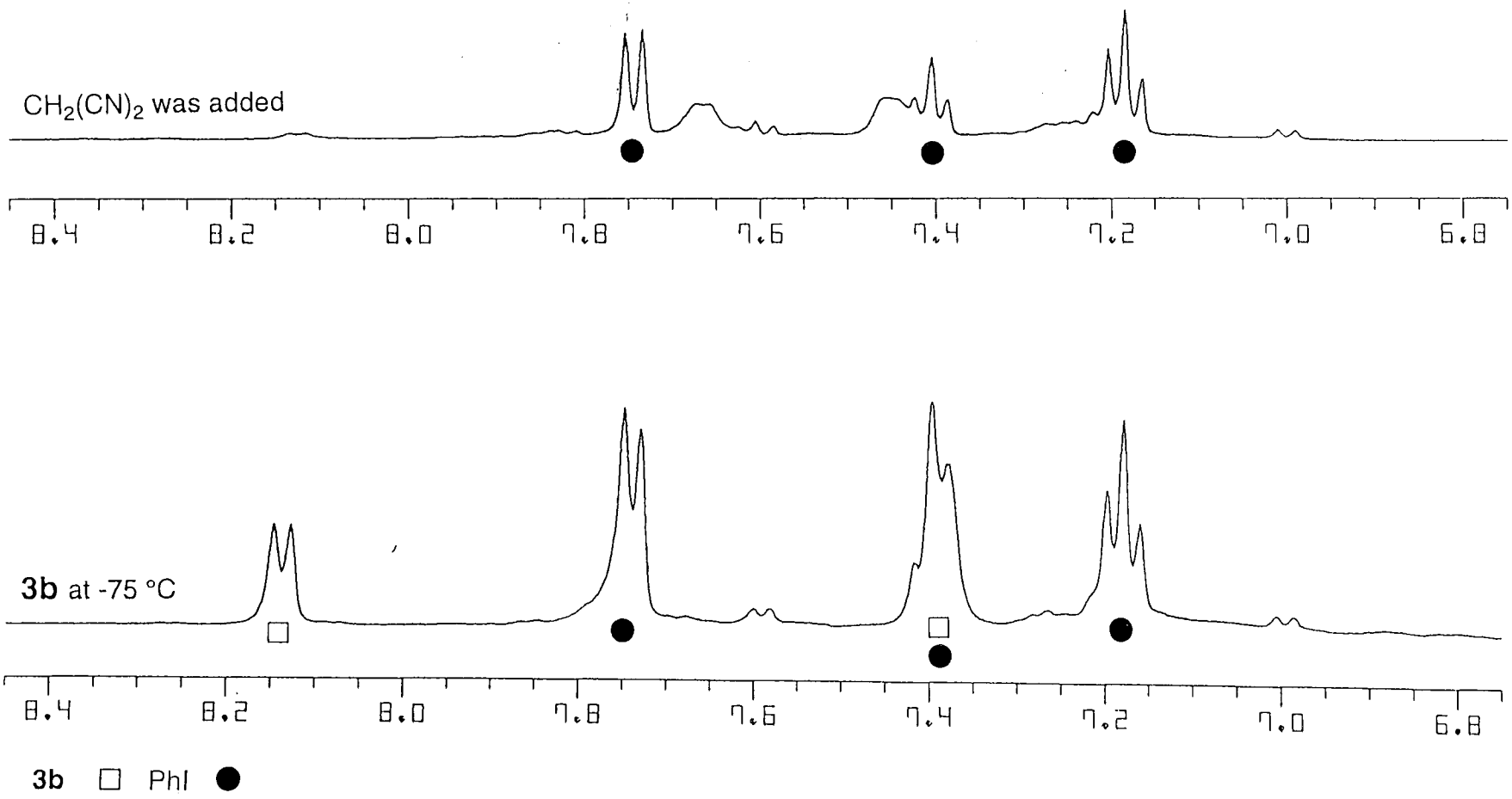


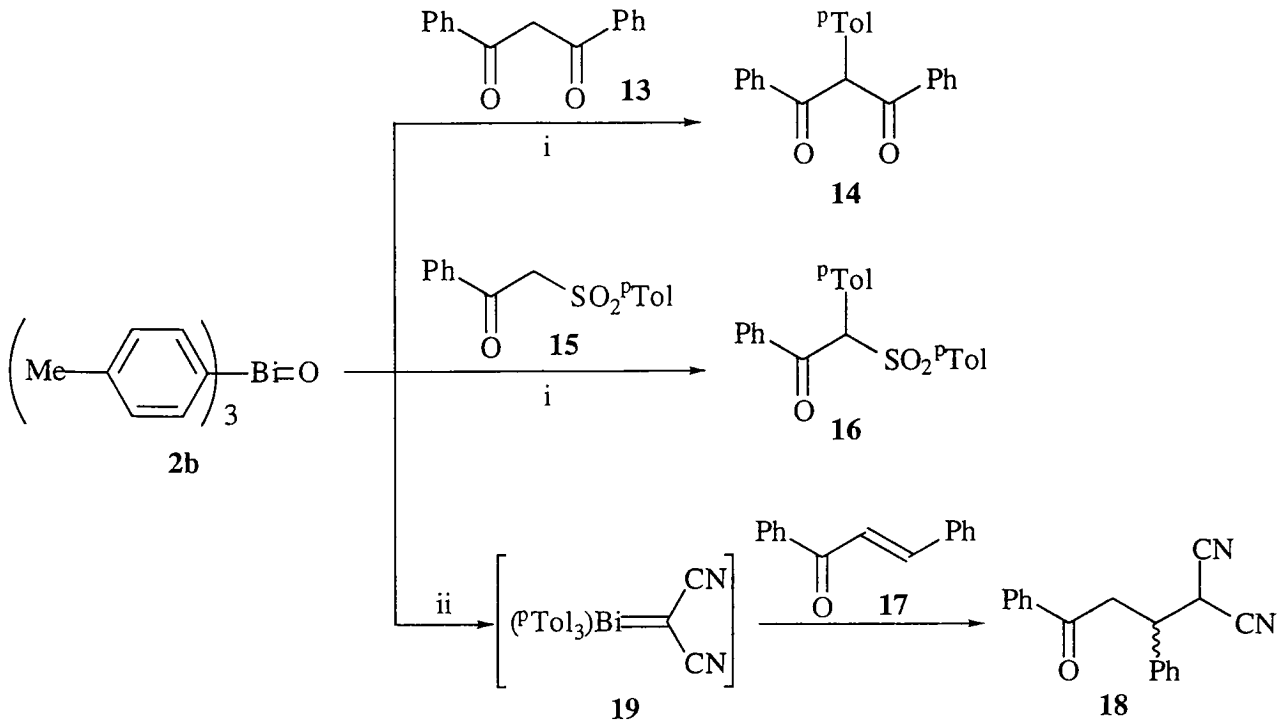
Substrate	Reaction time (h)	Product	Yield (%)
PhCH(OH)Me	2		86
	2		80
	2		100
	2		95
	2		75
PhNHNHPh	1	Ph−N≡N−Ph	52
Ph_3P	2	Ph_3P=O	100
	6		33*
	18	No Reaction	

* BF_3•OEt_2 (1.0 mmol) was added.

Then we examined the reaction between bismuthane oxide **2** with active methylene compounds such as dibenzoylmethane, malononitrile and nitromethane. Treatment of these substrates with a solution of the oxide **2b** led to the formation of a yellow or an orange suspension. In the case of dibenzoylmethane **13**, 2-(4-methylphenyl)-1,3-diphenylpropane-1,3-dione **14**[30] and bismuthane **3b** were obtained in 83 and 41% yield, respectively. Since unchanged dibenzoylmethane was recovered in 17%, no diarylated product was obtained. This is significanltly diffent from that the arylation reaction of active methylene compounds using hypervalent organobismuth compounds give di- or poly-arylated products.[31] The reaction between the oxide **2b** and dibenzoylmethane might proceed via abstraction of the acidic methylene proton to afford bismuth(V) intermediate **13**, which decomposed at room temperature to give an arylated product. Similarly, the oxide **2b** reacted with ω-(toluene-*p*-sulfonyl)acetophenone **15** to give the mono-arylated product **16** in moderate yield. While in the case of the reaction of oxide **2** with malononitrile, no such arylation products were obtained; the reaction mixture changed into characteristic red colour, however, complex mixture was obtained after usual work-up. This reaction was monitored by ^{1}H NMR in CD_2Cl_2 at -70 °C; the ArH peaks due to oxide **2b** completely changed into a pair of broad doublet at δ 7.45 and 7.67, which decomposed after warmed to room temperature (**Fig. 4**). The intermediate could not isolate due to its thermal unstability, however, it reacted with chalcone **17** to give product **18** via C-C bond formation at low temperature. Judging from these facts, the intermediate may be supposed as a bismuthonium ylide **19** (Scheme 4).

Fig.4 ^{1}H NMR (CD_2Cl_2) spectra of *in situ* generated $^{p}Tol_3Bi{=}O$ **3b** and its reaction with malononitrile at -75 °C.





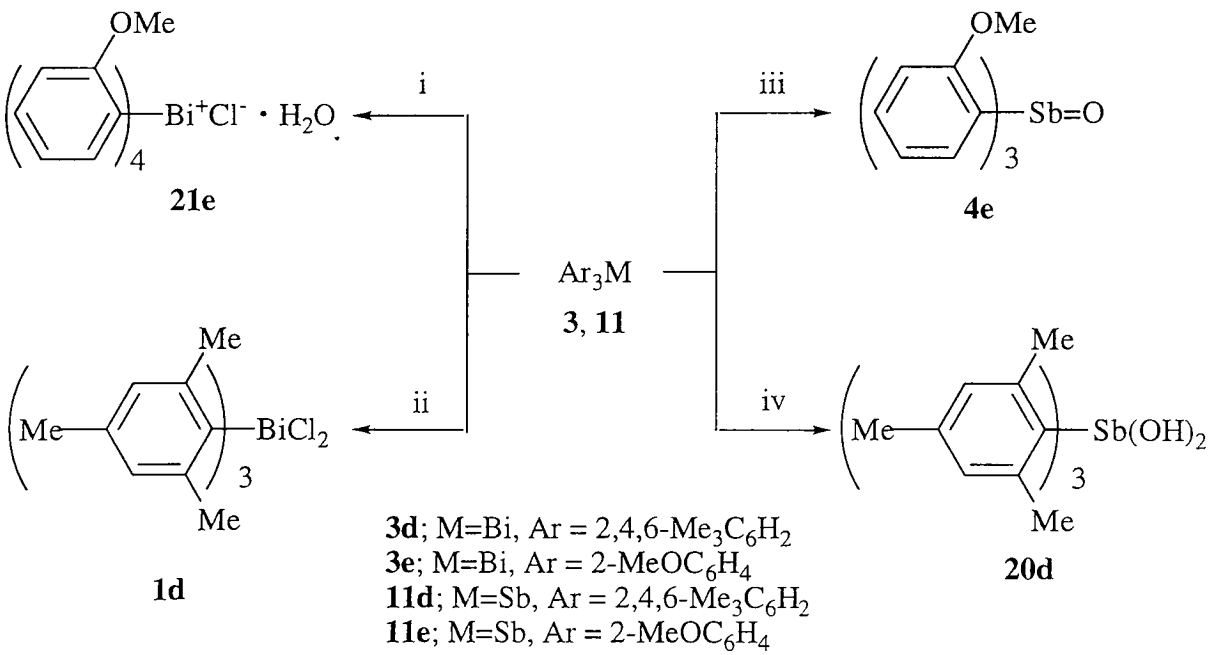
Scheme 4
Reagent and conditons: i, CH_2Cl_2, r.t.; ii, $H_2C(CN)_2$, CH_2Cl_2, -40 °C

Isolation of Triarylbismuthane Oxides

As descrived above, it is so difficult to isolate triarylbismuthane oxides **2a-c** under the atmospheric conditions, due to their high reactivity against carbon dioxide. Then we tried to isolate the oxides **2** by changing the aryl groups attached to bismuth centres. Mesityl group (2,4,6-trimethylphenyl group) was chosen for the steric protection group; trimesitylbismuthane **2d** was treated with iodosylbenzene in boiling dichloromethane, however, the major product was the corresponding dichloride **1d**. In chlorine free solvent such as benzene, the oxidation reaction did not proceed smoothly, and gave a complex mixture. This result is quite different that tirmesitylstibane **11d** is oxidized with iodosylbenzene to give its dihydroxide **20**[32a] in excellent yield.

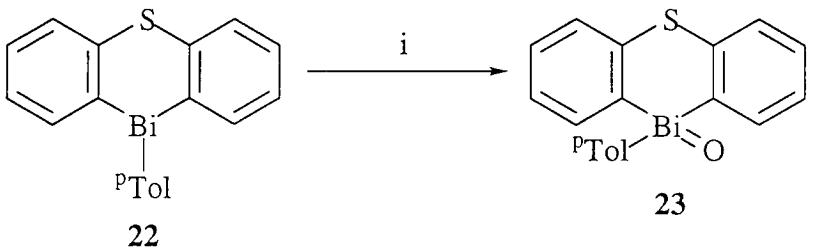
Tris-(4-fluorophenyl) and tris-(4-chlorophenyl)bismuthane were

not oxidized by iodosylbenzene; almost of the starting bismuthanes were recovered after the prolonged heating. The direct oxidation of tris-(2-methoxyphenyl)bismuthane **1e** in boiling dichloromethane led to the unexpected result; the product was tetrakis-(2-methoxyphenyl)bismuthounim chloride monohydrate **21**. It is the first example of the thermally stable bismuthonium salts containing chloride as counter anion. For detail of the reaction, see part 2 of this thesis. In the case of oxidation of tris-(2-methoxyphenyl)stibane **11e**, the corresponding oxide **4e**[32b] was obtained in quantitative yield. These differences of chemical behaviour of bismuthanes **3** and stibanes **11** toward oxidation may be caused due to difference of the reactivity of the corresponding oxides; bismuthane oxides **2** may be reactive enough to abstract chlorine atom from dichloromethane under the reaction condisions (Scheme 5).



Scheme 5
Reagent and conditons: i, PhI=O, CH_2Cl_2, 40 °C; ii, PhI=O, CH_2Cl_2, 35 °C,))); iii, PhI=O, C_6H_6, 80 °C; iv, PhI=O, CH_2Cl_2, r.t.

After several trials, we found that a heterocyclic bismuthane could stabilize the corresponding oxide effectively; treatment of 10-(4'-methylphenyl)phenothiabismine **22**[30] with iodosylbenzene in dichloromethane gave the corresponding oxide **23** as a yellow microcrystalline solid in quantitative yield (Scheme 6). FAB-MS spectrum of the oxide **23** exhibited a peak due to M+1 fragment. IR spectrum does not show any significant peaks due to sulfoxide function. Judging from the result of elemental analysis, it is supposed as a monohydrate, although the possibility of the dihydroxide can not be reuled out. In contrast to the previously prepared bismuthane oxides **2**, the oxide **23** can be handled under atmospheric conditions, and it is the first example of the isolable bismuthane oxide. The oxide **23** is soluble in dichloromethane, chloroform, 1,2-dichloroethane, and insoluble in acetonitrile, diethylether and hexane. Single crystals of oxide **23** for X-ray crystallographic study could be grown from a mixture of 1,2-dichloroethane–acetonitrile, however, the crystals become cloudy during handling under atmospheric conditions due to its efflorescence nature. We now trying to prepare good crystals for X-ray crystallographic study.



22 **23**

Scheme 6
Reagent and conditons: i, PhI=O, CH_2Cl_2, 40 °C

Interestingly, 10-(4'- methylphenyl)phenoxabismine **24**,[30] which

possess a similar structure to **22** does not produce the isolable bismuthane oxide. In addition, tris-(2-methylthiophenyl)bismuthane **3f**[33] was oxidized with iodosylbenzene to recover the unchanged bismuthane and thioanisole. These findings suggest that the six membered cyclic structure containing sulfur and bismuth might be essential for the stabilization of the bismuthane oxide **23**.

Experimental

Dichloromethane, toluene, ethyl acetate and chloroform were all distilled from calcium hydride under argon before use. Triarylbismuthanes **3a-f** were prepared by the reaction between bismuth(III) chloride and the corresponding arylmagnesium bromides. Iodosylbenzene was prepared according to the reported procedure,[34] and stored in refrigerator below -20 °C to avoid thermal disproportionation.[35] All mps were determined on a Yanagimoto hot stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer for solutions in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were obtained on a Shimadzu FTIR-8100 spectrophotometer. FAB-MS spectra were determined on a JEOL JMS HS 110 mass spectrometer. Elemental analyses were performed at Microanalytical Laboratory, Institute for Chemical Research, Kyoto University.

General procedure for the preparation of ^{1}H NMR sample of the bismuthane oxides 2

To a mixture of bismuthane **3** (12 mg , 25 μmol) and iodosylbenzene (7

mg, 33 μmol), solvent (ca. 1cm^3) was added and sonicated at 40 °C under argon untill a starting suspension turned into a clear solution. The resulting solution was used in further ^{1}H NMR experiment.

Reaction of bismuthane oxide 2b with bis-(*tert*-butyl dimethylsilyl)selenide. A solution of oxide **2b** (25 μmol) in toluene-d_8 was treated with excess of a solution of bis-(*tert*-butyl dimethylsilyl)selenide in $CDCl_3$. The broad peaks due to oxide **2b** changed into sharp peaks, which gradually turned into those of bismuthane **3b.**

***In situ* generation of triarylbismuthane oxides 2**

In toluene. General procedure: triarylbismuthane **3** (1.0 mmol) was added to a suspension of freshly prepared iodosylbenzene (286 mg, 1.3 mmol) in dry toluene (40 cm^3) and the resulting mixture was sonicated at 40 °C under argon on a commercial ultrasonic washing machine until bismuthane **2** was completely consumed (checked by TLC). Generally, it takes 2–3 h to complete the reaction. The resulting bright yellow solution was quickly filtered through a Celite bed, if needed. The FAB-MS spectrum of the filtrate (*m*-nitrobenzyl alcohol was used as a matrix) exhibited definite peaks due to fragment ions; for oxide **2a**, *m/z*; 1459 ($PhBi_6O_8$), 1382 (Bi_6O_8), 1295 ($Ph_2Bi_5O_6$), 1157 (Bi_5O_7), 993 ($PhBi_4O_5$), 751 ($PhBi_3O_3$), 691 (Bi_3O_4), 675 (Bi_3O_3), 592 ($Ph_3BiOCH_2C_6H_4NO_2$), 517(Ph_4Bi), 363 (Ph_2Bi), 286 (PhBi) and 209 (Bi); for oxide **2b**, *m/z*;1473 ($pTolBi_6O_8$), 1382 (Bi_6O_8), 1323 ($pTol_2Bi_5O_6$), 1157 (Bi_5O_7), 1007 ($pTolBi_4O_5$), 766 ($pTolBi_3O_3$), 691 (Bi_3O_4), 675 (Bi_3O_3), 634 ($pTol_3BiOCH_2C_6H_4NO_2$), 573 ($pTol_4Bi$), 391 ($pTol_2Bi$), 300 (pTolBi) and 209

(Bi).

In dichloromethane. General procedure. A mixture of triarylbismuthane **3** (1.0 mmol) and freshly prepared iodosylbenzene (286 mg, 1.3 mmol) in dry dichloromethane (40 cm^3) was heated at 40 °C under argon until bismuthane **2** was completely consumed (checked by TLC). Generally, it takes 1–2 h to complete the reaction. The resulting yellow solution was used further reaction.

Trapping reaction of bismuthane oxide 2a with benzoic anhydride

To a toluene solution (40 cm^3) of bismuthane oxide **2a**, was added a solution (3 cm^3) of benzoic anhydride (226 mg, 1 mmol) to give a yellow suspension, which was filtered and the filtrate was concentrated under reduced pressure. Recrystallization of the residue from benzene–hexane (1:4) gave triphenylbismuth dibenzoate **7** (450 mg, 66%), mp 172-174 °C (lit.[19] 169 °C); δ_H 7.30~7.48 (9 H, m), 7.58 (6 H, t, *J*8.0), 7.99 (4 H, d, *J*8.0) and 8.32 (6 H, d, *J* 8.0); ν_{max} (KBr)/cm^{-1} 1599, 1559, 1470, 1437, 1364, 984, 719 and 681.

Trapping reaction of bismuthane oxide 2a with toluene-*p*-sulfonic acid monohydrate

To a toluene solution (40 cm^3) of bismuthane oxide **2a**, was added an acetonitrile solution (5 cm^3) of toluene-*p*-sulfonic acid monohydrate (190 mg, 1 mmol) to afford a yellow solution. Usual work-up afforded triphenylbismuth bis(toluene-*p*-sulfonate) **8** (273 mg, 70%), mp 175-177 °C (lit.[20] 178 °C); δ_H 2.30 (6 H, s), 7.00 (4 H, d, J_{AB} 8.0), 7.22 (4 H, d, J_{AB} 8.0), 7.59 (3 H, t, *J*8.0), 7.72 (6 H, t, *J*8.0) and 8.18 (6 H, t, *J*8.0).

Preparation of polymeric bismuthane oxides

A toluene solution of bismuthane oxide **2a** (1 mmol) prepared by the above method was evaporated under reduced pressure till 5 cm^3. Addition of cold hexane (20 cm^3) to this solution gave cream yellow precipitates, which was washed with hexane (2 cm^3 x 3). This precipitates decomposed upon heating above 150 °C without showing a definite melting range (Found: C, 31.1; H, 2.3%. $C_{18}H_{15}BiO$ requires C, 47.4; H, 3.3%). By the similar procedure, polymeric oxide **2b** was prepared (Found: C, 38.43; H, 3.20%. $C_{21}H_{21}BiO$ requires C, 50.6; H, 4.2 %).

Reaction of polymeric bismuthane oxide 2b with triphenylphosphine

A mixture of polymeric bismuthane oxide **2b** (220 mg, estimated as 0.43 mmol of pure oxide), triphenylphosphane (110 mg, 0.43 mmol), and benzene (5 cm^3) was stirred at ambient temperature for 3 days. Insoluble powder was filtered off and the filtrate was separated by silica-gel column chromatography to give unchanged phosphane (35%), bismuthane **3b** (159 mg, 57%) and triphenylphosphane oxide (78 mg, 65%), respectively.

Reaction of polymeric bismuthane oxide 2a with dimedone To a mixture of polymeric oxide **2a** (137 mg, estimated as 0.3 mmol of oxide) and dimedone (36 mg, 0.26 mmol), was added dichloromethane (10 cm^3) and heated at reflux for 3 h. The resulting suspension was filtered and the filtrate was concentrated under reduced pressure to give orange residue (40 mg), in which contained bismuthonium ylide **9**.[22] The yield of the

ylide **9** was estimated as 55 % by ^{1}H NMR spectroscopy.

Reaction of bismuthane oxide 2b with boron trifluoride etherate

To a solution of bismuthane oxide **2b**, prepared from bismuthane **3b** (482 mg, 1.0 mmol) and iodosylbenzene (264 mg, 1.2 mmol) in CH_2Cl_2 (30 cm^3), was added boron trifluoride etherate (0.12 cm^3, 1.0 mmol) at -60 °C, and the reaction mixture was warmed to room temperature. The mixture was stirred at room temperature for 1 day, and the insoluble precipitate was filtered off throgh a Celite bed. The filtrate was concentrated to leave a brown solid, which was chromatographed on silica-gel using CH_2Cl_2-EtOH (1 : 0 to 100 : 5) to give tris-(4-methylphenyl)bismuth dichloride **1b** (50 mg, 9%) and tetrakis-(4-methylphenyl)bismuthonium tetrafluoroborate **10b** (162 mg, 24%). *Compound* **10b**; mp 205-207 °C; δ_H 2.44 (12 H, s), 7.49 (8 H, d, J_{AB} 8.0) and 7.63 (8 H, d, J_{AB} 8.0); ν_{max} (KBr)/cm^{-1} 1487, 1446, 1391, 1312, 1281, 1209, 1188, 1121, 1061, 1005, 799, 519 and 475; *m/z* (FAB) 573 (pTol$_4$Bi), 391 (pTol$_2$Bi) and 300 (pTolBi) (Found: C, 50.73; H, 4.15. $C_{28}H_{28}BBiF_4$ requires C, 50.93; H, 4.27%).

Reaction of bismuthane oxide 2c with boron trifluoride etherate

To a solution of bismuthane oxide **2c**, prepared from tris-(4-methoxyphenyl)bismuthane **3c** (530 mg, 1.0 mmol) and iodosylbenzene (440 mg, 2.0 mmol) in CH_2Cl_2 (50 cm^3), was added boron trifluoride etherate (0.7 cm^3, 5.8 mmol) at -60 °C, and the reaction mixture was warmed to room temperature. The mixture was stirred vigorously with aqueous sodium

tetrafluoroborate (3 g) at room temperature for 2 h. Organic phase was separated, and the aqueous layer was extracted with CH_2Cl_2 (5 cm^3 X 3). The extracts were combined and dried ($MgSO_4$), and filtered. The filtrate was concentrated to leave a brown oil, which was chromatographed on silica-gel using CH_2Cl_2-EtOH (1 : 0 to 100 : 5) to give tetrakis-(4-methoxyphenyl)bismuthonium tetrafluoroborate **10c** (45 mg, 6%). *Compound* **10c**; mp 174-175 °C; δ_H 3.85 (12 H, s), 7.20 (8 H, d, J_{AB} 8.8) and 7.65 (8 H, d, J_{AB} 8.1); δ_C 55.5 (MeO-), 118.0, 125.1 (Bi-C), 136.8 and 162.7; ν_{max}(KBr)/cm^{-1} 1580, 1568, 1489, 1458, 1296, 1254, 1179, 1121, 1050, 1017, 822, 521 and 513 (Found: C, 46.64; H, 3.85. $C_{28}H_{28}BiBF_4O_4$ requires C, 46.43; H, 3.90%).

Preparation of triphenylstibane oxide

A mixture of triphenylstibane **11a** (353 mg, 1.0 mmol), iodosylbenzene (220 mg, 1.0 mmol) and dry chloroform (20 cm^3) was sonicated at ambient temperature for 1 h to give the expected stibane oxide **4a**. Usual workup followed by recrystallization from hexane-chloroform (3:1; 20 cm^3) afforded compound **4a** as colourless crystals (310 mg, 84%), mp 219-221 °C (lit.[16] 220-222 °C). δ_H 7.28-7.42 (9 H, m) and 7.66-7.82 (6 H, m); ν_{max} (KBr)/cm^{-1} 1478, 1433, 1064, 739, 727, 692, 668, 656, 650, 476 and 453; *m/z* 506, 504 ($Ph_3SbOCH_2C_6H_4NO_2$), 490, 488 (Ph_3Sb_2O), 431, 429 (Ph_4Sb), 371, 369 (Ph_3SbO), 277, 275 (Ph_2Sb) and 200, 198 (PhSb).

Metathesis reaction between dichloride 1b and silver(I) oxide

To a benzene solution (30 cm^3) of tris-(4-methylphenyl)bismuth

dichloride **1b** (554 mg, 1 mmol), was added an aqueous suspension (5 cm^3) of silver(I) oxide, freshly prepared from 308 mg of silver nitrate and 80 mg of sodium hydroxide, and the resulting suspension was stirred vigorously at ambient temperature for 7 h in the dark. The resulting light grey suspension was filtered through a Celite bed, and the organic layer was separated, dried (Na_2SO_4), and concentrated to afford pale yellow crystals (220 mg), mp 105–107 °C. ^{1}H NMR spectrum of the solid showed the product was a mixture of bismuthane **3b** and μ-oxybis-{tris-(4-methylphenyl)bismuth} dichloride as follows; δ_H 2.32 (9 H, s, $^pTol_3Bi$), 2.41 (18 H, s, μ-oxy), 7.19 (6 H, d, J_{AB} 8.0, $^pTol_3Bi$), 7.43 (12 H, d, J_{AB} 8.0, μ-oxy), 7.62 (6 H, d, J_{AB} 8.0, $^pTol_3Bi$) and 8.29 (12 H, d, J_{AB} 8.0, μ-oxy); ν_{max} (KBr)/cm^{-1} 1483, 1389, 1308, 1182, 1113, 1003, 793, 617 and 474; *m/z* 648 ($^pTol_3Bi(O)OCH_2C_6H_4NO_2$), 544 ($^pTol_2BiOCH_2C_6H_4NO_2$), 517 ($^pTol_3BiCl$), 391 ($^pTol_2Bi$), 300 ($^pTolBi$) and 209 (Bi).

Oxidation reaction using bismuthane oxide

General procedure. To a toluene solution (40 cm^3) of bismuthane oxide **2** (1 mmol), was added a substrate (0.8 mmol) in the same solvent (5 cm^3) at ambient temperature, and the resulting mixture was stirred for several hours. The resulting suspension was filtered through a Celite and the filtrate was concentrated to leave an oily residue, which was separated by silica-gel column chromatography using hexane-ethyl acetate (1:0 to 20:1) as an eluent.

***sec*-Phenetyl alcohol**

Treatment of oxide the **2b** (1 mmol) with *sec*-phenetyl alcohol (100 mg, 0.8 mmol) at room temperature for 4 h gave bismuthane **3b** (201 mg, 42%) and acetophenone (82 mg, 86%).

Cinnamil alcohol

Treatment of oxide the **2b** (1 mmol) with cinnamil alcohol (107 mg, 0.8 mmol) at room temperature for 12 h gave bismuthane **3b** (240 mg, 50%) and cinnamaldehyde (84 mg, 80%).

4-Methoxybenzyl alcohol

Treatment of oxide the **2b** (1 mmol) with 4-methoxybenzyl alcohol (111 mg, 0.8 mmol) at room temperature for 12 h gave bismuthane **3b** (160 mg, 33%) and 4-methoxybenzaldehyde (108 mg, 100%).

Benzoin

Treatment of oxide the **2b** (1 mmol) with benzoin (170 mg, 0.8 mmol) at room temperature for 12 h gave bismuthane **3b** (121 mg, 25%) and benzil (159 mg, 95%).

Benzopinacol

Treatment of oxide the **2b** (1 mmol) with benzopinacol (366 mg, 1.0 mmol) at room temperature for 2 h gave bismuthane **3b** (390 mg, 81%), unchanged benzopinacol (91 mg, 25%) and benzophenone (270 mg, 75%).

Hydrazobenzene

Treatment of oxide the **2b** (1 mmol) with hydrazobenzene (147 mg, 0.8 mmol) at room temperature for 1 h to give a mixture(248 mg) of bismuthane **3b** (36%) and azobenzene (52%). The yield was estimated by ^{1}H NMR.

Triphenylphosphane

Treatment of oxide the **2b** (0.48 mmol) with cinnamil alcohol (125 mg,

0.48 mmol) at room temperature for 2 h gave bismuthane **3b** (160 mg, 69%) and triphenylphosphane oxide (133 mg, 100%).

2-(4-Methoxyphenyl)-1,3-dithiolane

Treatment of oxide the **2b** (1 mmol) with 2-(4-methoxyphenyl)-1,3-dithiolane (170 mg, 0.8 mmol) at room temperature for 12 h, however no reaction occured (checked by TLC). To the reaction mixture, was added boron trifluoride etherate (0.12 cm^3, 1.0 mmol) to give unchanged dithiolane (99 mg, 58%) and 4-methoxybenzaldehyde (37 mg, 33%).

Reaction between bismuthane oxide 2b and dibenzoylmethane 13

To a solution (40 cm^3) of bismuthane oxide **2b** (1 mmol) in CH_2Cl_2, was added dibenzoylmethane **13** (224 mg, 1 mmol) in the same solvent (6 cm^3), and stirred at ambient temperature for 4 h. Resulting pale yellow suspension was filtered through a Celite bed and the filtrate was concentrated to give yellow residue, which was separated by silica-gel column chromatography using hexane- ethyl acetate (1:0 to 7:1) as an eluent to give bismuthane **3b** (197 mg, 41%), recovered compound **13** (38 mg, 17%) and 2-(4'-methylphenyl)-1,3-diphenylpropane-1,3-dione **14** (260 mg, 83%). The latter compound was pale yellow crystals, mp 146–149 °C (lit., [30] 147–150 °C); δ_H 2.33 (3 H, s), 6.53 (1 H, s), 7.19 (2 H, d, J_{AB} 8.0), 7.27 (2 H, d, J_{AB} 8.0), 7.43 (4 H, t, J_{AB} 8.0), 7.55 (2 H, t, J_{AB} 8.0) and 7.98 (4 H, d, J_{AB} 8.0); *m/z* 314 (M^+), 236 (M-Ph), 209 (M-PhCO), 105 (PhCO) and 91 ($^pTol^+$). Treatment of compound **13** (224 mg, 1 mmol) with bismuthane oxide **2b** (1 mmol) in toluene at ambient temperature for 7 h gave the bismuthane **3b** (220 mg,

46%), recovered **13** (67 mg, 30%) and product **14** (220 mg, 70%) after the same work-up.

Reaction between bismuthane oxide 2b and ω-toluene-*p*-sulfonyl acetophenone 15

To a solution (40 cm^3) of bismuthane oxide **2b** (1 mmol) in CH_2Cl_2, was added ω-toluene-*p*-sulfonyl acetophenone **15** (274 mg, 1 mmol) in the same solvent (10 cm^3), and stirred at ambient temperature for 12 h. Resulting yellow suspension was filtered through a Celite bed and the filtrate was concentrated to give yellow oil, which was separated by silica-gel column chromatography using hexane- ethyl acetate (1:0 to 7:1) as an eluent to give bismuthane **3b** (288 mg, 60%), recovered compound **15** (130 mg, 48%) and ω-(4'-methylphenyl)-ω-(toluene-*p*-sulfonyl)acetophenone **16** (116 mg, 32%). *Compound* **16**; mp 145–146 °C; δ_H 2.33 (3 H, s), 2.42 (3 H, s), 6.08 (1 H, s), 7.10 (2 H, d, J_{AB} 7.8), 7.20–7.24 (4 H, m), 7.40 (2 H, t, *J*7.4), 7.50–7.55 (3 H, m) and 7.86 (2 H, d, J_{AB} 8.6); ν_{max}(KBr)/cm^{-1} 1682, 1315, 1221, 1143, 1086, 982, 687, 575 and 530; *m/z* 364 (M^+), 209 (M - $pTolSO_2$), 182 (M - 2pTol) and 105 (PhCO).

Reaction between bismuthane oxide 2b and malononitrile

Without trapping reagent. To a CH_2Cl_2 solution (30 cm^3) of bismuthane oxide **2b** (1 mmol), was added maronontrile (66 mg, 1.0 mmol) in the same solvent (10 cm^3), and stirred at room temperature for 12 h. Resulting red solution changed into a brown suspension, which was filtered through a Celite bed and the filtrate was concentrated to give brown oil,

which was separated by short silica-gel column chromatography using CH_2Cl_2 as an eluent to give a mixture (350 mg) of iodobenzene (45%), bismuthane **3b** (36%) and dichloride**1b** (10%). The yield of the products was estimated by ^1H NMR.

In the presence of charcone. To a CH_2Cl_2 solution (30 cm^3) of bismuthane oxide **2b** (1 mmol), was added marononitrile (66 mg, 1.0 mmol) in the same solvent (10 cm^3) at -40 °C, and stirred at the same temperature for 30 min. To the resulting reddish orange solution, was added a solution of charcone **17** (208 mg, 1.0 mmol) in CH_2Cl_2 (5 cm^3) at -40 °C, and the mixture was allowed to warm to room temperature. The mixture was stirred at the same temperature for 12 h, filtered through a Celite bed and the filtrate was concentrated to give bown oil, which was separated by silica-gel column chromatography using hexane–ethyl acetate (1 : 0–10 : 1) to give iodobenzene (78 mg, 32%), bismuthane **3b** (130 mg, 27%), charcone **17** (64 mg, 31%) and 1,3-diphenyl-4,4-dicyanobutane-1-one **18** (189 mg, 69%), mp 127–128 °C (lit.,[36] 125–126 °C); δ_H 3.68 (1 H, d, *J* 6.1), 3.70 (1 H, d, *J* 7.7), 3.92–4.01 (1 H, m), 4.77 (1 H, d, *J* 4.5), 7.41-7.70 (8 H, m) and 7.98 (2 H, d, *J* 9.0).

Oxidation of trimesitylbismuthane 3d

A mixture of trimesitylbismuthane **3d** (283 mg, 0.5 mmol) and iodosylbenzene (132 mg, 0.6 mmol) in CH_2Cl_2 (20 cm^3) was sonicated at 35°C for 1.5 h to afford a bright yellow solution, which was filterd through a Celite bed. The filtrate was concentrated under reduced pressure, and diluted with hexane to deposit pale yellow crystals of trimesitylbismuth dichloride **1d** (271 mg,

85%), mp 130 °C (decomp.); δ_H 2.31 (9 H, s), 2.72 (18 H, s) and 7.14 (6 H, s); ν_{max}(KBr)/cm^{-1} 3013, 1568, 1453, 1293, 980, 936, 849 and 538 (Found: C, 50.33; H, 5.24. $C_{27}H_{33}BiCl_2$ requires C, 50.94; H, 5.19%).

Oxidation of trimesitylstibane 11d

A mixture of trimesitylstibane **11d** (479 mg, 1.0 mmol) and iodosylbenzene (242 mg, 1.1 mmol) in CH_2Cl_2 (30 cm^3) was stirred at room temperature for 3 h to afford a charky suspension, which was filterd through a Celite bed. The filtrate was concentrated under reduced pressure to give trimesitylstibane dihydroxide **20** (490 mg, 99%), mp 182–184 °C (lit.,[32b] 202 °C, DTA); δ_H 2.30 (9 H, s), 2.57 (18 H, s) and 6.97 (6 H, s); δ_C 21.0, 24.7, 130.0, 139.7, 142.1 and 142.2; ν_{max}(KBr)/cm^{-1} 3642, 3480 (br), 2963, 1599, 1559, 1455, 1289, 1026, 847, 586, 519 and 492 (Found: C, 63.52; H, 6.94. $C_{27}H_{35}SbO_2$ requires C, 63.26; H, 6.89 %).

Oxidation of tris-(2-methoxyphenyl)bismuthane 3e

Tris-(2-methoxyphenyl)bismuthane **3e** (530 mg, 1.0 mmol) and freshly prepared iodosylbenzene (440 mg, 2 mmol) were suspended in CH_2Cl_2 (50 cm^3) and heated at reflux until **3e** was consumed. The resulting suspension was filtered through a Celite bed to remove any insoluble materials and the filtrate was concentrated under reduced pressure to give an oily residue. Ethyl acetate (20~30 cm^3) was added to the residue and separated microcrystalline solid of tetrakis-(2-methoxyphenyl)bismuthonium chloride monohydrate **21**. Further crystallization from CH_2Cl_2-EtOAc (1 : 5) gave pure compound **21** (469 mg, 68%); mp 195–197 °C (dec.); δ_H

2.19 (2 H, br s), 3.67 (12 H, s), 7.22~7.32 (8 H, m) and 7.55~7.75 (8 H, m); δ_C 56.46, 112.59, 124.50, 127.20 (Bi-C), 134.20, 134.79 and 159.74; ν_{max}(KBr)/cm^{-1} 3450 (br), 1472, 1433, 1277, 1242, 1043, 785 and 760; *m/z* (FAB) 637 (Ar_4Bi), 423 (Ar_2Bi), 316 (ArBi) and 209 (Bi) (Found: C, 48.84; H, 4.28. $C_{28}H_{30}BiClO_5$ requires C, 48.66; H, 4.34 %).

Oxidation of tris-(2-methoxyphenyl)stibane 11e with iodosylbenzene

A mixture of tris-(2-methoxyphenyl)stibane **11e** (443 mg, 1 mmol), iodosylbenzene (242 mg, 1.1 mmol,) and benzene (50 cm^3) was heated at reflux for 1h to give a pale yellow suspension, which was filtered through a Celite bed while hot. The filtrate was concentrated under reduced pressure to give a mixture (556 mg) of iodobenzene and tris-(2-methoxyphenyl)stibane oxide **4e**. Trituration of this mixture with hexane gave a pure oxide **4e** (454 mg, 99 %), mp 247–249 °C (lit.,[32a] 247 °C); δ_H 3.78 (9 H, s), 7.00 (3 H, dd, *J* 8.3, 1.0), 7.12 (3 H, dt, *J* 7.4, 1.0), 7.44 (3 H, ddd, *J* 8.3, 7.4, 1.7) and 7.88 (3 H, dd, *J* 7.4, 1.7).

Oxidation of 10-(4'-methylphenyl)phenothiabismine 22

A mixture of 10-(4'-methylphenyl)phenothiabismine **22**[30] (242 mg, 0.5 mmol) and freshly prepared iodosylbenzene (165 mg, 0.75 mmol) in CH_2Cl_2 (30 cm^3) was heated at reflux for 1.5 h. The resulting suspension was filtered through a Celite bed to remove any insoluble materials and the filtrate was concentrated under reduced pressure to leave a yellow solid. The residue was recrystallized from a mixture of CH_2Cl_2–hexane to give 10-(4'-

methylphenyl)phenothiabismine-Bi-oxide monohydrate **23** (225 mg, 90%), mp 166–167 °C; δ_H 2.32 (3 H, s), 7.22 (2 H, d, J_{AB} 8.1), 7.27 (2 H, dt, *J* 7.4 and 1.4), 7.44 (2 H, dt, *J* 7.4 and 1.4), 7.75 (2 H, dd, *J* 7.4 and 1.4), 8.03 (2 H, d, J_{AB} 8.1) and 8.45 (2 H, dd, *J* 7.4 and 1.4); δ_C 21.4, 129.9, 130.2, 131.1, 132.4, 134.2, 136.4, 140.5, 140.9, 150.3 and 161.8; ν_{max}(KBr)/cm^{-1}; 3400 (br), 1482, 1426, 1183, 1090, 1009, 795, 770, 750, 569, 473, 446 and 415; *m/z* (FAB) 501 (M+1), 485 {(M-O)+1}, 394 (M-pTol-O), 300 (pTolBi) and 209 (Bi) (Found: C, 44.61; H, 3.05. $C_{19}H_{17}BiO_2S$ requires C, 44.02; H, 3.28 %).

Oxidation of 10-(4'-methylphenyl)phenoxabismine 24

A mixture of 10-(4'-methylphenyl)phenoxabismine **24**[30](94 mg, 0.2 mmol) and iodosylbenzene (66 mg, 0.3 mmol) in CH_2Cl_2 (10 cm^3) was heated at reflux for 1 h. The resulting suspension was filtered through a Celite bed to remove any insoluble materials and the filtrate was concentrated under reduced pressure to leave an orange oil (80 mg), which was a complex mixture.

Oxidation of tris-(2-methylthiophenyl)bismuthane 3f

A mixture of tris-(2-methylthiophenyl)bismuthane **3f**[33] (289 mg, 0.5 mmol) and iodosylbenzene (165 mg, 0.75 mmol) in CH_2Cl_2 (25 cm^3) was heated at reflux for 25 min. The resulting suspension was filtered through a Celite bed to remove any insoluble materials and the filtrate was concentrated under reduced pressure to leave an orange oil (286 mg), which contained iodosylbenzene (50%), starting bismuthane **3f** (62%) and thioanisole (16%). The yield of products was estimated by ^{1}H NMR.

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Chapter 2 Unexpected Formation of Highly Stabilized Tetrakis-(2-alkoxyphenyl)bismuthonium Salts in the Oxidation of Tris-(2-alkoxyphenyl)bismuthanes with Iodosylbenzene

Abstract

Treatment of tris-(2-alkoxyphenyl)bismuthanes **1** with iodosylbenzene in methylene dichloride at 40 °C led to none of the expected bismuthane oxides **2** but, quite unexpectedly, tetrakis-(2-alkoxyphenyl)bismuthonium chlorides **3** in moderate to good yields. In some cases, bismuthonium formates **4** accompanied the reaction. A similar treatment in benzene in the presence of benzyl bromide, ethyl bromide, or 2,2,2-trifluoroethyl iodide led to the corresponding bismuthonium bromides **7** and iodides **8**. Through the anion exchange, a variety of bismuthonium salts including formate **4**, tetrafluoroborate **11**, toluene-*p*-sulfonate **12**, bromide **7**, iodide **8** and perchlorate **13** were prepared from the salt **3** in good yields. In contrast to the known tetraphenylbismuthonium salts, all of these new bismuthonium salts exhibited high thermal stability. The molecular structure of compound **7a** was elucidated by X-ray analysis, where the four neighbouring oxygen atoms are found to surround the bismuth atom tetrahedrally via a weak through-space interaction with the metal, making the bismuth centre less susceptible to the nucleophilic attack of the halide anion.

Introduction

In contrast to well documented triorganylpnicogen oxides derived from lighter 15 group elements, $R_3Pn{=}O$ (Pn = N, P, As and Sb), the oxides of triorganylbismuthanes remain to be characterized yet.[1] This

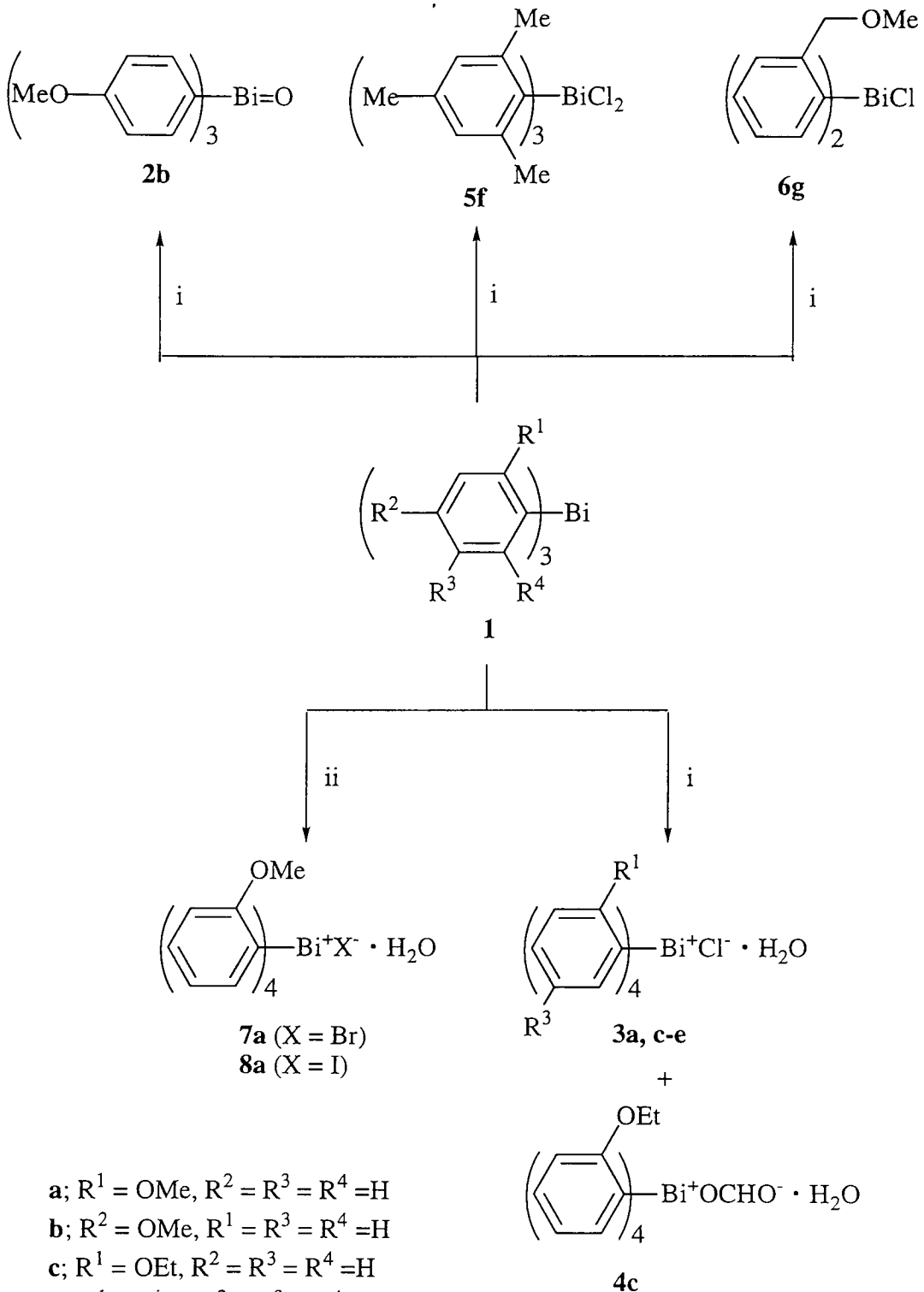
class of compounds are of interest because of their high potential as precursor to a variety of organobismuth(V) compounds. However, the literature to date contains only a few papers dealing with somewhat conflicting results. Many attempts by previous workers to obtain triarylbismuthane oxides by direct oxidation of triarylbismuthanes **1** have so far met with failure; attempted oxidation of triphenylbismuthane with hydrogen peroxide,[2] dinitrogen trioxide,[3] potassium permanganate,[4] selenium dioxide,[5] and cyclic nitrones[6] all led to none of the expected product.

Recently, we have found that iodosylbenzene was effective as the oxidant for this purpose; under ultrasonic irradiation or gentle heating in an appropriate organic solvent, some triarylbismuthanes were smoothly converted to the corresponding oxides in good yield.[7] However, we could not isolate these oxides due to their high sensitivity toward moisture and carbon dioxide; during the course of evaporation under reduced pressure, the oxides were readily decomposed to intractable polymeric substances.

Results and Discussion

Since the 2- and 2, 6-dimethoxy-phenyl groups have been shown by PM3 calculation to stabilize the bismuthonium cation more effectively than the phenyl or 4-methoxyphenyl group,[8] we came to an idea of obtaining tris-(2-methoxyphenyl)bismuthane oxide **2a** by the oxidation of tris-(2-methoxyphenyl)bismuthane **1a** with iodosylbenzene, expecting that the 2-alkoxyphenyl ligand might work effectively to stabilize the polar bismuth oxide function. Treatment of bismuthane **1a** with an excess of iodosylbenzene in boiling methylene dichloride led to rapid disappearance of the oxidizing

agent to give an orange-coloured solution or suspension. Evaporation of the solution under reduced pressure left a brown oily residue which, much to our delight, could be crystallized out from CH_2Cl_2-Et_2O as a light brown solid. More conveniently, the reaction mixture was concentrated to a syrup, which was diluted with ethyl acetate to separate the same compound as a microcrystalline solid melting at 195-197 °C with decomposition. Elemental analysis of this compound showed a composition $C_{28}H_{30}BiClO_5$. Its ^{1}H-NMR spectrum in $CDCl_3$ exhibited a broad 2H absorption at around δ 2.2, a singlet due to the methoxy group at δ 3.66, and two peak clusters at around δ 7.22~7.32 and 7.55–7.75 due to aromatic protons. The broad resonance at high field suggests the presence of one water molecule, which was confirmed by an IR absorption at 3450 cm^{-1}. ^{13}C-NMR spectrum exhibited absorptions at δ 56.46, 112.59, 124.50, 127.20 (Bi-C), 134.20, 134.79 and 159.74 (MeO-C), showing the presence of four intact 2-methoxyphenyl moieties. A peak at δ 127.20, assigned to the *ipso* carbon attached to the bismuth atom, shifted 15.6 ppm upfield as compared with that of parent bismuthane **1a**. Such noticeable upfield shift of the signal due to the *ipso* carbon atom attached to a positively charged heteroatom centre is generally observed for various heteroatom onium compounds.[9] Thus the new compound may safely be formulated as a bismuthonium compound **3a**, $(2\text{-}MeOC_6H_4)_4BiCl{\bullet}H_2O$, which was further supported by a fast atom bombardment (FAB) mass spectrum showing diagnostic fragment peaks at *m/z* 637 (Ar_4Bi), 423 (Ar_2Bi), 316 (ArBi), and 209 (Bi). Formation of **3a** in a hydrated form may be attributed to adventitious water in commercial solvent used for workup.



a; R^1 = OMe, R^2 = R^3 = R^4 =H
b; R^2 = OMe, R^1 = R^3 = R^4 =H
c; R^1 = OEt, R^2 = R^3 = R^4 =H
d; R^1 = O^{i}Pr, R^2 = R^3 = R^4 =H
e; R^1 = OMe, R^2 = H, R^3 = Me, R^4 =H
f; R^1 = R^2 = R^4 =Me, R^3 = H
g; R^1 = CH_2OMe, R^2 = R^3 = R^4 =H

Scheme 1 *Reagents and conditions:* i, PhI=O, CH_2Cl_2, 40 °C; ii, PhI=O, RX (EtBr, $PhCH_2Br$, CF_3CH_2I), PhH, 40~50 °C

The present new oxidation reaction of triarylbismuthane was highly dependent on the solvent system employed; in chloroform, only a trace amount of the onium salt **3a** was obtained and 50 % of bismuthane **1a** was recovered intact, while in 1,2-dichloroethane the salt **3a** was obtained in 43 % yield. In benzene, the reaction did not proceed in the expected way; anisole and iodobenzene were the major products with a recovery of 59 % bismuthane **1a**, no other organobismuth compounds being detected in the product mixture. Since iodosylbenzene is known to disproportionate to iodoxybenzene and iodobenzene on heating,[10] low-boiling methylene dichloride was apparently the solvent of choice. Even in the presence of added water, the oxidation in methylene dichloride proceeded smoothly to give the onium salt **3a** in a similar or slightly reduced yield.

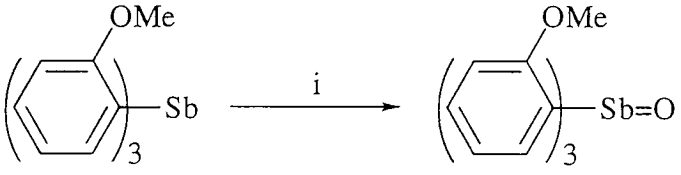
Tris-(2-ethoxyphenyl)bismuthane **1c**, tris-(2-isopropoxyphenyl)bismuthane **1d**, and tris-(2-methoxy-4-methylphenyl)bismuthane **1e** were all similarly oxidized by the present procedure to give the corresponding bismuthonium chlorides **3c-e** in moderate yield (Scheme 1). In the case of bismuthane **1c**, however, bismuthonium formate **4c** was obtained as the major product. The **3c** : **4c** ratio was estimated as 1 : 3.3 by ^{1}H-NMR analysis. Tris-(4-methoxyphenyl)bismuthane **1b** and tris-(2-methylphenyl)bismuthane behaved quite differently toward iodosylbenzene under similar reaction conditions; the former was converted to a presumed oxide **2b**, while the latter resisted to oxidation. Interestingly, tris-(2,4,6-trimethylphenyl)bismuthane **1f** was converted to the corresponding dichloride **5f** in 80 % yield, while tris-(2-methoxymethylphenyl)bismuthane **1g** gave

the corresponding diarylchlorobismuthane, bis-(2-methoxymethylphenyl)bismuth chloride **6g** in 22 % yield.

From these findings, it became clear that the alkoxy grouping attached to the *ortho* position of the bismuth atom is indispensable to stabilize tetraarylbismuthonium salts **2** in the oxygen-transfer oxidation of bismuthanes **1** by iodosylbenzene.

The ozone oxidation of bismuthane **1a** was also examined; bismuthane **1a** was added to a solution of ozone in methylene dichloride at -40 °C and gradually warmed to room temperature to afford a mixture of unchanged bismuthane **1a** (44 %) and tris(2-methoxyphenyl)bismuth dichloride (23 %) **5a**. This result was similar to that observed in the ozone oxidation of triphenylbismuthane in methylene dichloride, in which triphenylbismuth dichloride was obtained in 42 % yield. Supposedly, this oxidation reaction would proceed via the intermediacy of a bismuthane ozonide.[11]

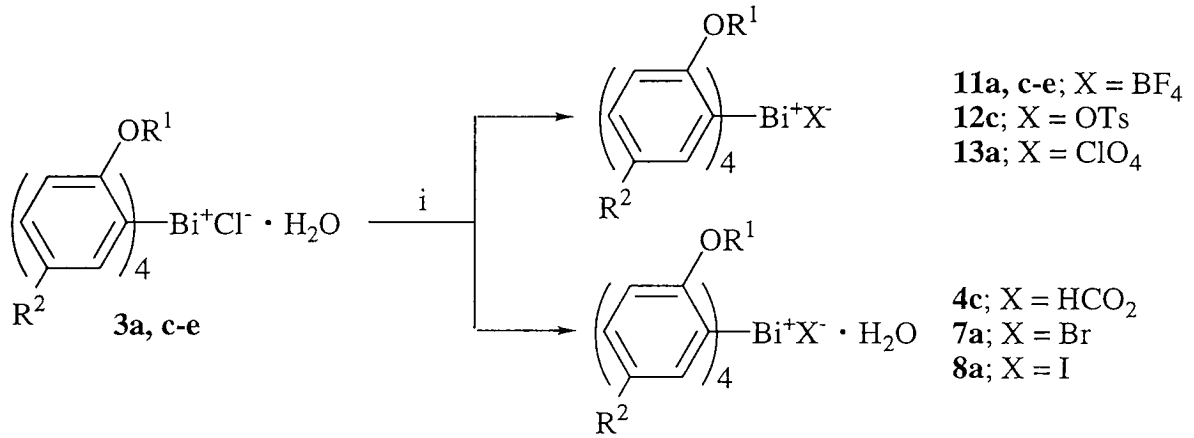
It would be pertinent to mention herein that tris-(2-methoxyphenyl)stibane **9** was smoothly oxidized with iodosylbenzene in benzene at reflux to give the expected oxide **10**[12] in almost quantitative yield (Scheme 2). Stibane oxides are more stable against moisture as compared with the corresponding bismuthane oxides **2**.[7]



9 **10**

Sheme 2
Reagents and conditions: i, PhI=O, PhH, 80 °C

Onium salts **2** are readily soluble in methylene dichloride, chloroform, acetone, acetonitrile and ethanol, but almost insoluble in ethyl acetate, ether, hexane and benzene. When chlorides **3a, c-e** were treated with silver(I) tetrafluoroborate in acetonitrile, the corresponding tetrafluoroborates **11a, c-e** were obtained in good yield (Scheme 3). Similarly, the chloride **3c** was converted to the formate **4c** and tosyl ester **12c** by treatment with an aqueous solution of sodium formate or tosylate. All of these new bismuthonium compounds **3a, c-e**, **4c**, **11a, c-e** and **12c** were thermally stable; they did not show any significant sign of degradation after 3 months storage under ambient conditions.



a; R^1 = Me, R^2 = H; **c**; R^1 = Et, R^2 = H; **d**; R^1 = ^{i}Pr, R^2 = H; **e**; R^1 = Me, R^2 = Me

Scheme 3
Reagents and conditions: i, MX ($AgBF_4$, HCO_2Na, NaOTs, NaBr, NaI or $AgClO_4$), water–CH_2Cl_2($CHCl_3$), room temp.

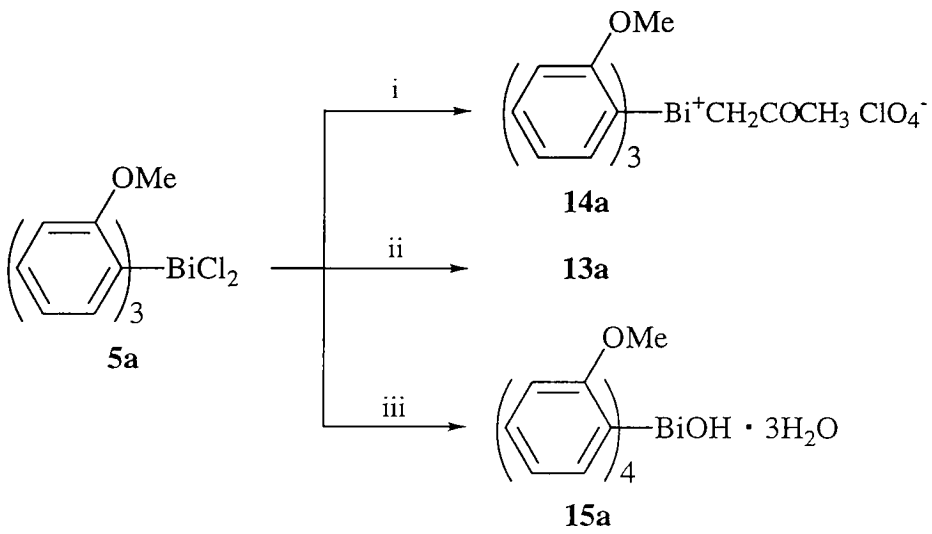
The first preparation of tetraphenylbismuthonium chloride and bromide was reported by Wittig and co-workers, who obtained them by treating pentaphenylbismuth with hydrogen chloride or bromine.[13] They described that these salts decomposed within several minutes at room temperature, producing the triphenylbismuthane and corresponding

halobenzenes. Hence, all stable bismuthonium salts so far known carry low-nucleophilic, bulky counter anions such as perchlorate, tetrafluoroborate, trifluoromethanesulfonate, and tetraphenylborate.[14-18] Beaumont and Goel have prepared a variety of bismuth(V) compounds, Ph_4BiX, by anion exchange reaction between tetraphenylbismuthonium chloride and appropriate metal salts.[14] They observed that the nature of Ph_4BiX changes depending on the anions involved; when X was ClO_4, BF_4 or PF_6, the compounds showed an ionic nature, while X was NO_3, Cl_3CCO_2, NCO or NCS, they took a non-ionic pentacoordinate structure. X-Ray crystallographic study of tetraphenylbismuthonium perchlorate demonstrated that the bismuth centre possesses a tetrahedral onium structure.[15] When X was N_3 or NCSe, the corresponding Bi(V) compounds were thermolabil at room temperature and readily decomposed to triphenylbismuthane and others.

We were also successful in obtaining the isolable bismuthonium bromide **7** and iodide **8** from the chloride **3** by the anion exchange. Shaking a chloroform solution of bismuthonium salt **3a** with an aqueous sodium bromide gave the corresponding bromide **7a** as crystals in 74 % yield. A similar treatment with sodium iodide gave the iodide **8a** in 74 % yield. Both salts **7a** and **8a** are remarkably stabilized and decompose only above 200 °C. Similarly to the chloride **3a** and tetrafluoroborate **11a**, they do not show any sign of degradation when stored at room temperature. Compounds **7a** and **8a** constitute the first example of tetraarylbismuthonium halides of indefinite shelf life. These halides were also readily available by the oxidation of bismuthane **1a** with iodosylbenzene in benzene in the presence of corresponding alkyl halides; bismuthane **1a** was oxidized in

the presence of ethyl or benzyl bromide at 40~50 °C to give compound **7a** in 39 and 42 % yields, respectively. In the latter case, the formation of benzaldehyde as by-product was observed. A similar oxidation of bismuthane **1a** in the presence of 2,2,2-trifluoroethyl iodide afforded compound **8a** in 13 % yield (Scheme 1).

In connection with the anion exchange, the metathesis reaction of tris-(2-methoxyphenyl)bismuth dichloride **5a** with silver perchlorate was reexamined in acetone[18] and butan-2-one,[14] respectively. In acetone, tris-(2-methoxyphenyl)(2-oxopropyl) bismuthonium perchlorate **14a** was obtained in 55 % yield, while in butan-2-one, the formation of a dark tarry substance was predominant, tetrakis-(2-methoxyphenyl)bismuthonium perchlorate **13a** being obtained only in a slight amount (~1 %) (Scheme 4).



Scheme 4
Reagent and conditons: i, $AgClO_4$, Me_2CO, room temp. ;
ii, $AgClO_4$, MeCOEt, room temp. ; iii, Ag_2O, CH_2Cl_2, 40 °C

Treatment of the salt **14a** with brine gave bismuthane **1a** (100 %), probably via the intermediacy of a pentacoordinate bismuth compound. Metathesis of compound **5a** with silver(I) oxide in benzene-water gave bismuthane **1a** in a low yield, while the same reaction in methylene

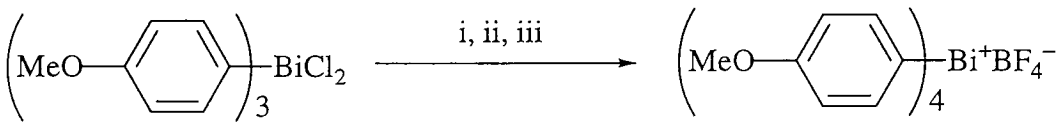
dichloride gave tetrakis-(2-methoxyphenyl)bismuthonium hydroxide **15a**, which probably arose from the metathesis of the initially formed chloride **3a** with silver(I) oxide. A trace amount of the formate **4a** was also detected by ^{1}H-NMR monitoring. The likely source of the formate anion is formaldehyde, derived from methylene dichloride according to the sequence shown in Scheme 6. By treatment with tetrafluoroboric acid in acetonitrile-water, hydroxide **15a** was converted to tetrafluoroborate **11a** in good yield. A similar conversion of iodonium chloride to the tetrafluoroborate has previously been reported.[19]

Onium salts **3a**, **7a**, **8a**, **11a** and **13a** were all similar in their ^{1}H- and ^{13}C-NMR and IR spectral patterns, although the salt **9a** showed additional broad IR absorption due to BF_4 anion (Table 1). IR spectrum of salt **4c** contained a strong carbonyl absorption at 1632 cm^{-1}, which falls within the carboxylate anion region, endorsing the ionic structure of salt **4c**. Spectral data showed that these bismuthonium salts have a similar ionic structure with a long separation between the bismuth atom and the corresponding anions, thereby the decomposition of these salts via a ligand coupling mode being suppressed.

Tetrakis-(4-methoxyphenyl)bismuthonium salt.

In order to get insight into the influence of the 2-alkoxyphenyl groups on the thermal stability of the corresponding bismuthonium salts, we prepared tetrakis-(4-methoxyphenyl)bismuthonium salts, and compared its chemical nature with those of tetrakis-(2-alkoxyphenyl)bismuthonium salts. By the action of 4- methoxyphenylmagnesium bromide, tris-(4-

methoxyphenyl)bismuth dichloride **5b** was converted to pentakis-(4-methoxyphenyl)bismuth, which was further treated with trifluoromethanesulfonic acid to give the corresponding bismuthonium salt.[20,21] The counter anion was changed into tetrafluoroborate by metathesis reaction to obtain tetrakis-(4-methoxyphenyl)-bismuthonium tetrafluoroborate **11b** in moderate yield (Scheme 5). ^{1}H NMR spectrum of salt **11b** showed peaks at δ_H 3.85 (12 H), 7.20 (8 H) and 7.65 (8 H), while ^{13}C NMR spectrum exhibited peaks due to MeO- and Bi-C carbon at δ_C 55.52 and 125.11, respectively. In contrast to ^{1}H NMR spectra of tetrakis-(2-alkoxyphenyl)bismuthonium salts as shown in Table 1, no high field shift of the methoxy proton was observed in the case of the salt **11b**. ^{13}C NMR spectrum of salt **11b** suggests that the electron density of the Bi-C carbon is not so different from those of 2-alkoxyphenyl moieties.



5b **11b**

Scheme 5 *Reagents:* i, 4-MeO-C_6H_4MgBr; ii, $Me_3SiOSO_2CF_3$, EtOH; iii $NaBF_4$

However, treatment of the salt **11b** with sodium chloride led to the complete decomposition of the bismuthonium salt, giving the corresponding bismuthane **1b** and 4-chloroanisole in almost quantitative yield. This fact strongly suggests that 4-methoxyphenyl group has no ability to stabilize the bismuthonium centre, and an interaction between oxygen and bismuthonium centre may be essential for the thermal stabilization of tetrakis-(2-alkoxyphenyl)bismuthonium salts.

X-Ray structure analysis of compound 7a

In order to get sight into the extraordinarily enhanced thermal stability of tetrakis-(2-alkoxyphenyl)bismuthonium salts, an X-ray crystallographic analysis was performed for compound **7a**. As shown in Fig.1 and Table 2, the bismuth centre has a tetrahedral geometry with the Bi-C bond lengths [2.194(8) - 2.207(9) Å] and C-Bi-C bond angles [105.9(3) - 114.7(3) °]. The values are in accordance those of the previously reported tetraarylbismuthonium salts.[15,21] Compound **7a** is subject to the interactions between Bi and four oxygen atoms and the intramolecular Bi-O distances are intermediate between the sum of covalent radii (2.10 Å) and that of the estimated van der Waals radii (3.72 Å).[22]

Table 2 Selected bond lengths (Å) and angles (°) for compound **7a**, with estimated standard deviations in parentheses.

Bond Length		Bond angle	
Bi-C(1)	2.201(9)	C(1)-Bi-C(8)	112.4(3)
Bi-C(8)	2.194(8)	C(1)-Bi-C(15)	105.9(3)
Bi-C(15)	2.203(9)	C(1)-Bi-C(22)	107.7(3)
Bi-C(22)	2.207(9)	C(8)-Bi-C(15)	114.7(3)
Bi•••Br	6.752(3)	C(8)-Bi-C(22)	107.7(3)
Bi•••O(1)	2.968(7)	C(15)-Bi-C(22)	108.2(3)
Bi•••O(2)	3.099(2)	Bi-C(1)-C(2)	114.2(6)
Bi•••O(3)	2.968(6)	Bi-C(1)-C(6)	124.0(7)
Bi•••O(4)	3.091(6)	Bi-C(8)-C(9)	116.7(7)
		Bi-C(8)-C(13)	121.6(7)
		Bi-C(15)-C(16)	115.0(7)
		Bi-C(15)-C(20)	124.0(7)
		Bi-C(22)-C(23)	117.0(7)
		Bi-C(22)-C(27)	122.1(7)
		O(1)-C(2)-C(1)	114.2(8)
		O(1)-C(2)-C(3)	127.0(9)
		O(2)-C(9)-C(8)	116.8(8)
		O(2)-C(9)-C(10)	125.4(9)
		O(3)-C(16)-C(15)	114.0(9)
		O(3)-C(16)-C(17)	125.9(9)
		O(4)-C(23)-C(22)	116.1(8)
		O(4)-C(23)-C(24)	124.6(9)

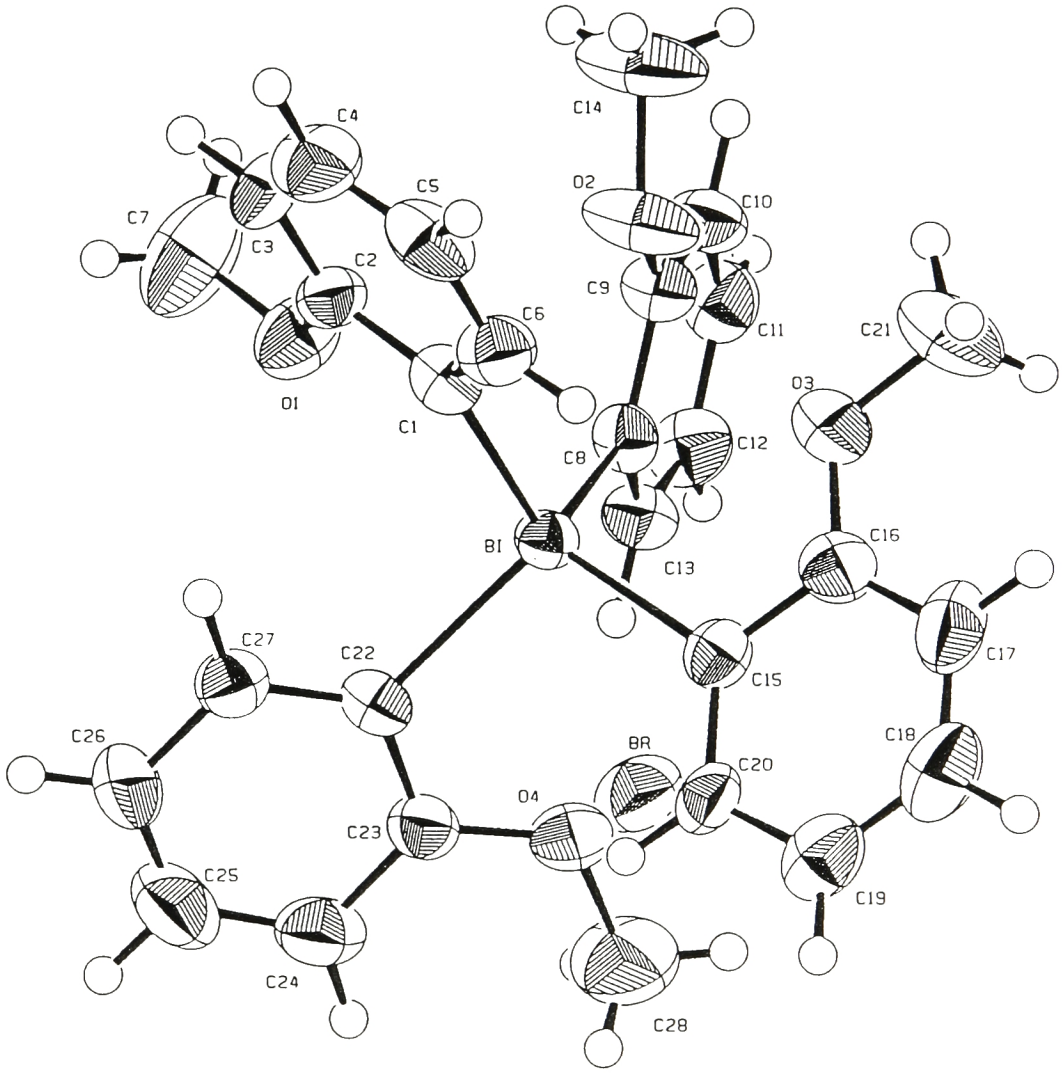


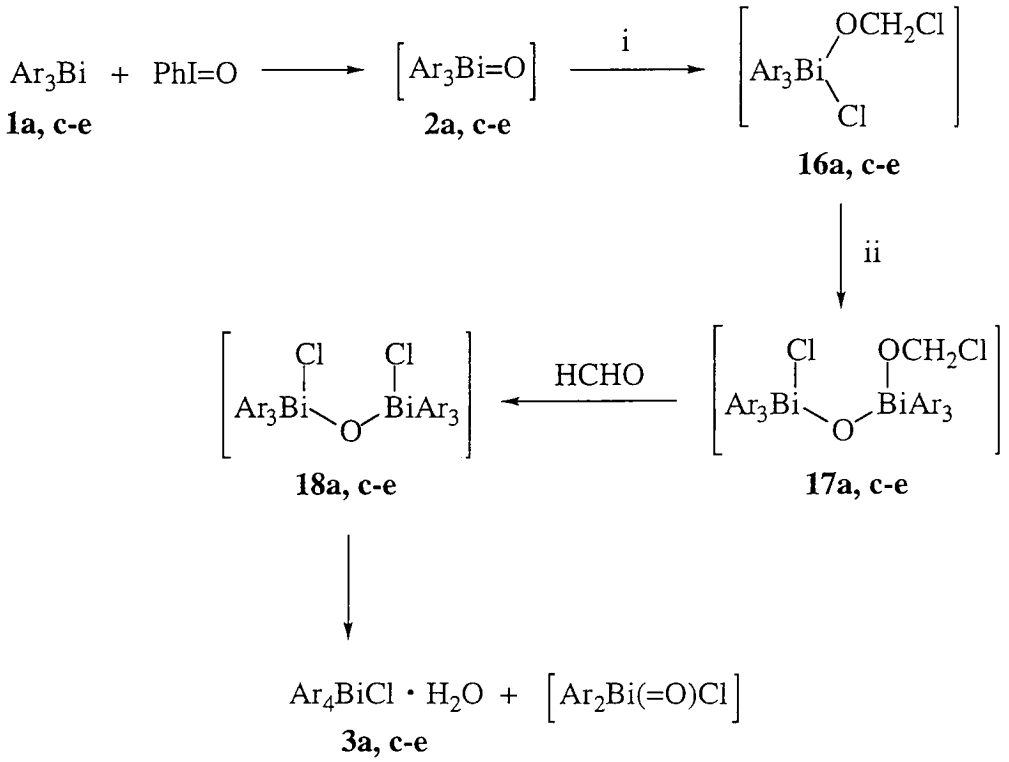
Fig. 1 ORTEP drawing of compound **7a**, with crystallographic numbering scheme. The percentage probability level of the ellipsoids in this drawing is 50%.

All methoxyl groups are found to lean slightly toward the bismuth atom with a deviation of about 5° from the standard sp^2 bond angle of 120°. A similar type of the Bi-O interaction has been observed for tris-(2,6-dimethoxyphenyl)bismuthane.[8] A large separation between the bismuth and bromine atoms [6.752(3) Å] is in accord with the ionic nature of compound **7a**. Since the previously reported bismuth-bromine covalent bond lengths are around 3 Å,[23] we may safely conclude that there is little or no direct interaction between the bismuthonium moiety and bromide anion.

A possible mechanism for the formation of bismuthonium salts 3.

The mechanism of the formation of the salt **3** is not clear at present. However, one possible pathway leading to compound **3** may be depicted as shown in Scheme 6. Of course, other possible mechanisms counld not be ruled out. Bismuthane **1a, c-e** undergoes oxygen-transfer reaction with iodosylbenzene to give the corresponding oxide **2 a, c-e** as the initial product, which is assumed to react with methylene dichloride to form a penta-coordinate intermediate **16a, c-e**. Insertion of another molecule of oxide **2** to the bisumuth-chlorine bond of this intermediate **16a, c-e** would result in the formation of a μ-oxo type intermediate **17a, c-e**. Elimination of a formaldehyde molecule from **17a, c-e** would give another μ-oxo type intermediate **18a, c-e**, in which one of the aryl groups may migrate toward the neighbouring bismuth atom to form bismuthonium chloride **3a, c-e**. The counterpart of the bismuth moieties is supposed to be transformed into triarylbismuthane **1a, c-e** and other products by subsequent

disproportionation reaction. Although the compounds of type **18** have been reported previously,[1a] their exact nature has not been established well to date. So we withhold detailed discussion on the mode of the formation of bismuthonium compounds **3a**, **c-e** at the present stage.



Scheme 6 *Reagents:* i, CH_2Cl_2; ii, $Ar_3Bi{=}O$

To further the above mechanistic considaration, the following experiments were carried out. First, possible involvement of aryl radical species is ruled out, since no aryl-aryl coupling products were detected from any of the present reactions; the oxidation proceeded smoothly even in the presence of a radical scavenger, 1,1-diphenylethylene. Oxidation of an equimolar mixture of bismuthanes **1a** and **1e** with excess iodosylbenzene gave a mixture of all four possible bismuthonium chlorides **3a**, **3e**, $Ar^1{}_3Ar^2BiCl$, and $Ar^1Ar^2{}_3BiCl$ (Ar^1 = 2-methoxy-4-methylphenyl, Ar^2 = 2-methoxyphenyl), as was confirmed by FAB-mass spectroscopy. This observation is consistent

with the formation and subsequent decomposition of the μ-oxo type intermediates **17** and **18**. The main product from the oxidation of bismuthane **1c**, was bismuthonium formate **4c** (*vide supra*). This result may be taken to support the elimination of a formyl moiety from the intermediate **17**. In accordance with this observation, benzaldehyde was detected in the oxidation of bismuthane **1a** with iodosylbenzene in benzene in the presence of benzyl bromide.† In the present oxidation leading to bismuthonium compounds, alkyl halide including methylene dichloride should have worked not only as a halide anion source but also as an oxygen acceptor.

The formation of bismuthonium salt **15a** in the metathesis reaction between dichloride **5a** and silver (I) oxide is also suggestive of the formation of the corresponding μ-oxo type intermediate **18**. The conversion of triarylbismuth dichlorides **5** to the corresponding μ-oxo type compounds have previously been reported by Goel and co-workers.[1a] However, Doak and co-workers had earlier reported that the reaction between triphenylbismuth dichloride and silver perchlorare in anhydrous ethanol gave a good yield of tetraphenylbismuthonium perchlorate.[17] Additional conflicting result, also reported by Goel,[14] suggests a possibility that the μ-oxo type compound **18** may be converted to the bismuthonium salt **3** under certain conditions. With an intent to verify the reaction pathway shown in Scheme 5, attempts to prepare the μ-oxybis{tris-(2-methoxyphenyl)bismuth} dichloride **18a** by a few different approaches including the anion exchange reaction of μ-oxybis{tris-(2-methoxyphenyl)bismuth} di(perchlorate) or di(triflate) have been made. As has been mentioned above, the reaction of dichloride **5a** with silver perchlorate gave three different type of products, **13a**, **14a** and

15a, but any expected μ-oxybis{tris-(2-methoxyphenyl)bismuth} di(perchlorate) could not be obtained. The reaction was carried out in a benzene-water mixture, a typical reaction condition to obtain a μ-oxo type compound from the corresponding dichloride; however, the product was bismuthonium salt **13a** in 18 % yield. A newly developed preparative method of μ-oxybis(trarylbismuth) di(trifrate)[24] was also applied to the present purpose; dichloride **5a** was treated successively with trimethylsilyl triflate and hexamethyldisiloxane, but the reaction gave a mixture of at least four compounds including bismuthonium salt (checked by ^{1}H-NMR). By treatment of this mixture with brine, we could isolate the bismuthonium salt **3a** by chromatography over silica gel. These findings are highly suggestive of the facile conversion of the μ-oxybis{tris-(2-methoxyphenyl)bismuth} derivative into tetrakis-(2-methoxyphenyl)bismuthonium salt. At present, the preparation of the μ-oxobis{tris-(2-methoxyphenyl)bismuth} compound is not successful and the development of more promising methodology for our purpose are under way.

Some of these stabilized bismuthonium salts have been found to exhibit a prominent *in vitro* antimicrobial activity against *Helicobacter pylori*, and relevant biological data will be published elsewhere.

Experimental

All oxidation reactions were carried out under an atmosphere of dry argon. All solvents were distilled from CaH_2 and stored over molecular sieves 4 Å. Triarylbismuthanes were prepared from the corresponding arylmagnesium bromides or aryllithiums with bismuth(III) chloride and recrystallized

from benzene-methanol. Iodosylbenzene was prepared according to the reported procedure[25] and stored at -20 °C. Other commercially available reagents were used without further purification. Column chromatography was performed on silica gel (Wakogel, 200 mesh). All mps were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Coupling constant *J* values are given in Hz. IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. FAB mass spectra were obtained on a JEOL JMS-HS 110 spectrometer using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at Microanalytical Laboratory, Institute of Chemical Research, Kyoto University.

Triarylbismuthanes

Compound 1a; mp 159-161 °C (lit.,[26] 167~169); δ_H 3.76 (9 H, s), 6.87 (3 H, dt, *J*7.3, 1.0), 6.99 (3 H, dd, *J*8.1, 1.0), 7.32 (3 H, ddd, *J*8.1, 7.3, 1.7) and 7.45 (3 H, dd, *J* 7.3, 1.7); δ_C 55.49, 109.73, 123.99, 129.12, 139.05, 142.81 (BiC_{ipso}) and 162.14.

Compound 1c; mp 123-124 °C (lit.,[27] 121-122); δ_H 1.25 (9 H, t, *J*7.0), 3.99 (6 H, q, *J*7.0), 6.85 (3 H, dt, *J*7.2, 1.0), 6.96 (3 H, dd, *J*8.1, 1.0), 7.28 (3 H, ddd, *J* 8.1, 7.2, 1.7) and 7.50 (3 H, dd, *J* 7.2, 1.7); δ_C 14.74, 63.74, 110.72, 123.75, 128.86, 139.09, 143.55 (Bi-C) and 161.49.

Compound 1d; mp 101-102 °C; δ_H 1.21 (18 H, d, *J*6.0), 4.50 (3 H, hept, *J*6.0), 6.82 (3 H, dt, *J*7.2, 1.0), 6.96 (3 H, d, *J*8.1), 7.25 (3 H, ddd, *J*8.1, 7.2, 1.7) and 7.53 (3 H, dd, *J*7.2, 1.7); δ_C 22.13, 70.01, 111.88, 123.55, 128.66,

139.56, 145.04 (Bi-C) and 160.47 (Found: C, 52.65; H, 5.44. $C_{27}H_{33}BiO_3$ requires C, 52.77; H, 5.41 %).

Compound 1e; mp 151-153 °C; δ_H 2.13 (9 H, s), 3.72 (9 H, s), 6.89 (3 H, d, *J* 8.2), 7.10 (3 H, ddd, *J* 8.2, 2.2, 0.7) and 7.29 (3 H, d, *J* 1.6); δ_C 20.59, 55.69, 109.63, 129.47, 132.84, 139.47, 142.5 (Bi-C) and 160.24 (Found: C, 50.42; H, 4.81. $C_{24}H_{27}BiO_3$ requires C, 50.35; H, 4.72 %).

Preparation of tetrakis-(2-alkoxyphenyl)bismuthonium chloride monohydrates 3

In methylene dichloride. General Procedure. Tris-(2-alkoxyphenyl)-bismuthane **1** (1 mmol) and freshly prepared iodosylbenzene (330~440 mg, 1.5~2 mmol) were suspended in methylene dichloride (50 cm^3) and heated to reflux until **1** was consumed (usually 0.5~1.5 h). When part of bismuthane **1** remained unchanged, additional amount of iodosylbenzene was introduced to complete the reaction. The resulting solution or suspension was filtered through a Celite bed to remove any insoluble materials and the filtrate was concentrated under reduced pressure to give an oily residue. Ethyl acetate (20~30 cm^3) was added to the residue and separated microcrystalline salt **3** was collected, washed with a minimum amount of the same solvent, and dried *in vacuo*. Further crystallization from CH_2Cl_2-EtOAc (1 : 5) gave pure compound **3**, the yield of which was calculated on the basis of bismuth.

In chloroform. Typical Procedure. Tris-(2-methoxyphenyl)bismuthane **1a** (530 mg, 1 mmol) and freshly prepared iodosylbenzene (330 mg, 1.5 mmol) were suspended in chloroform

(30 cm^3) and heated to reflux for 3 h. The resulting white suspension was filtered through a Celite bed to remove any insoluble materials and the filtrate was evaporated under reduced pressure to give a product (476 mg), the composition of which was estimated by ^{1}H-NMR as follows; **3a** (0.01 mmol), anisol (0.48 mmol), 2-chloroanisol (0.1 mmol), iodobenzene (0.67 mmol), and **1a** (0.57 mmol).

Tetrakis-(2-methoxyphenyl)bismuthonium chloride monohydrate 3a. Yield, 68 %; mp 195-197 °C (dec.); δ_H 2.19 (2 H, br s), 3.67 (12 H, s), 7.22~7.32 (8 H, m) and 7.55~7.75 (8 H, m); δ_C 56.46, 112.59, 124.50, 127.20 (Bi-C), 134.20, 134.79 and 159.74; ν_{max}(KBr)/cm^{-1} 3450 (br), 1472, 1433, 1277, 1242, 1043, 785 and 760; *m/z* (FAB) 637 (Ar_4Bi), 423 (Ar_2Bi), 316 (ArBi) and 209 (Bi) (Found: C, 48.84; H, 4.28. $C_{28}H_{30}BiClO_5$ requires C, 48.66; H, 4.34 %).

Tetrakis-(2-ethoxyphenyl)bismuthonium chloride monohydrate 3c. A product mixture from a similar oxidation of bismuthane **1c** was dissolved in chloroform (20 cm^3) and stirred vigorously with brine (20 cm^3) for 1 h. Organic layer was separated and aqueous layer was extracted with chloroform (10 cm^3 x 4). The combined extracts were dried ($MgSO_4$) and evaporated to give salt **3c** (28 %). Mp 212-214 °C (dec.); δ_H 0.81 (12 H, t, *J*7.0), 2.65 (2 H, br s), 3.98 (8 H, q, *J*7.0), 7.18~7.30 (8 H, m) and 7.55~7.75 (8H, m); δ_C 13.72, 64.97, 112.69, 124.20, 127.19 (Bi-C), 134.21, 134.86 and 159.15; ν_{max}(KBr)/cm^{-1} 3450 (br), 1482, 1464, 1443, 1277, 1242, 1044, 1032 and 762; *m/z* (FAB) 693 (Ar_4Bi), 451 (Ar_2Bi), 330 (ArBi) and 209 (Bi) (Found: C, 49.84; H, 5.31. $C_{32}H_{38}BiClO_5$ requires C, 51.42; H, 5.09 %).

Tetrakis-(2-isopropoxyphenyl)bismuthonium chloride monohydrate 3d. Yield, (39 %); mp 225-227 °C (dec.); δ_H 0.84 (24 H, d, *J* 6.0), 2.17 (2 H, br s), 4.60 (4 H, hept, *J*6.0), 7.15~7.25 (8 H, m) and 7.55~7.75 (8 H, m); δ_C 20.96, 71.13, 113.01, 123.72, 128.31 (Bi-C), 134.11, 135.58 and 157.96; ν_{max}(KBr)/cm^{-1} 3450 (br), 1582, 1468, 1443, 1275, 1240, 1125, 1103, 947 and 758; *m/z* (FAB) 749 (Ar_4Bi), 479 (Ar_2Bi), 344 (ArBi) and 209 (Bi) (Found: C, 53.80; H, 5.68. $C_{36}H_{46}BiClO_5$ requires C, 53.83; H, 5.73 %).

Tetrakis-(2-methoxy-4-methylphenyl)bismuthonium chloride dihydrate 3e. Yield, (29 %); mp 210-212 °C (dec.); δ_H 2.19 (4 H, br s), 2.34 (12 H, s), 3.62 (12 H, s) 7.18 (4 H, broad d, *J*8) 7.30 (4 H, br s) and 7.43 (4 H, br d, *J*8); ν_{max}(KBr)/cm^{-1} 3450 (br) 1487, 1281, 1250, 1146, 1042, 1011, 806 and 729 (Found: C, 50.46; H, 5.10. $C_{32}H_{40}BiClO_6$ requires C, 50.26; H, 5.23 %).

Oxidation of tris-(2-methoxymethylphenyl)bismuthane 1g

A mixture of tris-(2-methoxymethylphenyl)bismuthane **1g** (572 mg, 1 mmol), iodosylbenzene (330 mg, 1.5 mmol) and methylene dichloride (50 cm^3) was heated to reflux for 1 h to obtain a bright yellow coloured solution, which was filtered through a Celite bed and the filtrate was evapoated off to leave a brown residue (910 mg), which was chromatographed on alumina, using CH_2Cl_2 as the eluent to give unchanged bismuthane (40 %) and bis-(2-methoxymethylphenyl)bismuth chloride **6g** (22 %), mp 140-142 °C; δ_H 3.45 (6 H, s), 4.60 (2 H, d, *J*12), 4.78 (2 H, d, *J*12), 7.33~7.55 (6 H, m) and 8.59 (2 H, d, *J*7.6); ν_{max}(KBr)/cm^{-1} 1453, 1208, 1088, 1046, 957, 760 and 737 (Found: C, 39.90; H, 3.87. $C_{16}H_{18}BiClO_2$ requires C, 39.47; H, 3.70 %).

Ozone oxidation of bismuthane 1a in methylene dichloride

Ozonized oxygen (10 mmol h^{-1}) was passed into methylene dichloride (50 cm^3) at -70 °C for 1h to obtain a blue solution, to which was added bismuthane **1a** (530 mg, 1 mmol) in the same solvent (15 cm^3) in one portion. The resulting pale yellow suspension was allowed to warm to room temperature during the course of 30 min to give an orange-coloured suspension, which was filtered through a Celite bed. The filtrate was evaporated off under reduced pressure to leave a brown residue, which was chromatographed on silica gel, using CH_2Cl_2-EtOH (1 : 0 ~50 : 1) as the eluent, to give unchanged bismuthane **1a** (224 mg, 44 %) and tris-(2-methoxyphenyl)bismuth dichloride **5a** (137 mg, 23 %). *Compound* **5a**; mp 196-197 °C; δ_H 3.87 (9 H, s), 7.20~7.28 (6 H, m), 7.50 (3 H, dt, *J*7.7, 1.5) and 8.13 (3 H, dd, *J*8.2, 1.6); δ_C 56.33, 113.36, 123.34, 132.53, 133.44, 151.65 and 157.65; ν_{max}(KBr)/cm^{-1} 1588, 1472, 1431, 1273, 1248, 1046, 1019, 1001 and 750 (Found: C, 42.22; H, 3.51. $C_{21}H_{21}BiCl_2O_3$ requires C, 41.95; H, 3.52 %). This compound was also prepared by treating bismuthane **1a** with sulfuryl chloride in methylene dichloride at 0 °C. Tris-(2-ethoxyphenyl)bismuth dichloride **5c** was similarly obtained. *Compound* **5c**; mp 190 °C (decomp.); δ_H 1.10 (9 H, t, *J*7.0), 4.14 (6 H, q, *J*7.0), 7.15~7.30 (6 H, m), 7.46 (3 H, t, *J*7.9) and 8.13 (3 H, d, *J*8.4); ν_{max}(KBr)/cm^{-1} 1584, 1480, 1466, 1441, 1397, 1279, 1248, 1163, 1125, 1044, 1003, 922 and 758 (Found: C, 44.73; H, 4.20. $C_{24}H_{27}BiCl_2O_3$ requires C, 44.81; H, 4.23 %).

Oxidation of tris-(2- methoxyphenyl)stibane 9 with

iodosylbenzene

A mixture of tris-(2-methoxyphenyl)stibane **9** (443 mg, 1 mmol), iodosylbenzene (242 mg, 1.1 mmol,) and benzene (50 cm^3) was heated to reflux for 1h to give a pale yellow suspension, which was filtered through a Celite bed while hot. The filtrate was concentrated under reduced pressure to give a mixture (556 mg) of iodobenzene and tris-(2-methoxyphenyl)stibane oxide **10**. Trituration of this mixture with hexane gave a pure oxide **8** (454 mg, 99 %). *Compound* **10**, mp 247-249 °C (lit.,[12b] 247 °C); δ_H 3.78 (9 H, s), 7.00 (3 H, dd, *J*8.3, 1.0), 7.12 (3 H, dt, *J*7.4, 1.0), 7.44 (3 H, ddd, *J*8.3, 7.4, 1.7) and 7.88 (3 H, dd, *J*7.4, 1.7).

Preparation of bismuthonium tetrafluoroborates 11

An acetonitrile solution (5 cm^3) of silver(I) tetrafluoroborate (200 mg) was added to a solution of salt **3a** (517 mg, 0.75 mmol) in the same solvent (10 cm^3) and the resulting mixture was stirred in the dark under ambient conditions. After 2 h silver(I) chloride was filtered off and the filtrate was evaporated to leave a brown solid, which was extracted with methylene dichloride (10 cm^3 x 3). The combined extracts were evaporated and then treated with EtOAc (20 cm^3) to give tetrakis-(2-methoxyphenyl)bismuthonium tetrafluoroborate **11a** (468 mg, 86 %) as fine colourless crystals. *Compound* **11a**; mp 268-270 °C; δ_H 3.66 (12 H, s), 7.22~7.32 (8 H, m) and 7.55~7.75 (8 H, m); δ_C 56.49, 112.67, 124.60, 127.40 (Bi-C), 134.28, 134.94 and 159.92; ν_{max}(KBr)/cm^{-1} 1472, 1433, 1279, 1244, 1097, 1061, 1009 and 762 (Found: C, 46.00; H, 3.84. $C_{28}H_{28}BBiF_4O_4$ requires C, 46.43; H, 3.90 %). *Compound* **3c** (0.154 mmol, 115 mg) was similarly converted to

compound **11c** (87 %, 104 mg). Compounds **3d** (0.138 mmol, 111 mg) and **3e** (0.25 mmol, 186 mg) gave the corresponding tetrafluoroborates **11d** (107 mg, 92 %) and **11e** (156 mg, 80 %), respectively, as fine crystals.

Tetrakis-(2-ethoxyphenyl)bismuthonium tetrafluoroborate 11c. Mp > 300 °C; δ_H 0.80 (12 H, t, *J*7.0) 3.98 (8 H, q, *J*7.0), 7.15~7.30 (8 H, m) and 7.50~7.70 (8 H, m); δ_C 13.73, 64.99, 112.73, 124.20, 127.28 (Bi-C), 134.21, 134.90 and 159.25; ν_{max}(KBr)/cm^{-1} 1584, 1466, 1445, 1279, 1063, 1040 and 772 (Found: C, 48.95; H, 4.62. $C_{32}H_{36}BBiF_4O_4$ requires C, 49.25; H, 4.65 %).

Tetrakis-(2-isopropyloxyphenyl)bismuthonium tetrafluoroborate 11d. Mp > 300 °C; δ_H 0.83 (24 H, d, *J* 6.1) 4.60 (4 H, hept, *J* 6.1), 7.15~7.25 (8 H, m) and 7.55~7.75 (8 H, m); δ_C 20.96, 71.10, 113.00, 123.67, 128.30 (Bi-C), 134.08, 135.57 and 157.97; ν_{max}(KBr)/cm^{-1} 1584, 1468, 1277, 1242, 1125, 1105, 1055, 1038, 947 and 754 (Found: C, 51.63; H, 5.28. $C_{36}H_{44}BBiF_4O_4$ requires C, 51.69; H, 5.30 %).

Tetrakis-(2-methoxy-4-methylphenyl)bismuthonium tetrafluoroborate 11e. Mp 183-184 °C; δ_H 2.33 (12 H, s) 3.61 (12 H, s), 7.17 (4 H, d, *J*8.4) 7.31 (4 H, br s) and 7.43 (4 H, ddd, *J*8.4, 1.8, 0.7); δ_C 20.70, 56.45, 112.32, 127.15 (Bi-C), 134.25, 134.59 134.74 and 157.82; ν_{max}(KBr)/cm^{-1} 1601, 1487, 1441, 1279, 1248, 1150, 1097, 1061, 1011, 820 and 729 (Found: C, 49.06; H, 4.60. $C_{32}H_{36}BBiF_4O_4$ requires C, 49.25; H, 4.65 %).

Preparations of bismuthonium formate 4c, tosyl ester 12c, bromide 7a and iodide 8a

Tetrakis-(2-ethoxyphenyl)bismuthonium formate monohydrate 4c. To a solution of compound **3c** (52 mg, 0.07 mmol) in chloroform (15 cm^3) was added an aqueous solution (5 cm^3) of sodium formate (1 g) and the resulting mixture was stirred vigorously for 2 h at room temperature. Organic layer was separated and aqueous layer was extracted with chloroform (5 cm^3 x 4). The combined organic phase was dried ($MgSO_4$) and evaporated to give formate **4c** (37 mg, 70 %). *Compound* **4c**; mp 153-155 °C (dec.); δ_H 0.81 (12 H, t, *J* 7.0), 3.84 (2 H, br s), 3.97 (8 H, q, *J* 7.0), 7.18~7.30 (8 H, m) 7.55~7.75 (8 H, m) and 8.80 (1 H, s); ν_{max}(KBr)/cm^{-1} 1632, 1582, 1461, 1443, 1277, 1242, 1044 and 762 (Found: C, 52.92; H, 5.47. $C_{33}H_{39}BiO_7$ requires C, 52.38; H, 5.16 %).

Tetrakis-(2-ethoxyphenyl)bismuthonium toluene-*p*-sulfonate 12c. Similarly obtained from compound **3c** (192 mg, 0.257 mmol) and sodium tosylate (0.68 g per 15 cm^3). The product was chromatographed on silica gel, using CH_2Cl_2-EtOH (1 : 0~10 : 1) as an eluent, to give tosylate **12c** (152 mg, 68 %). Mp 272-273 °C; δ_H 0.79 (12 H, t, *J* 7.0), 2.29 (3 H, s), 3.97 (8 H, q, *J* 7.0), 7.09 (2 H, d, J_{AB} 8.3), 7.15~7.28 (8 H, m), 7.55~7.75 (8 H, m) and 7.90 (2 H, d, J_{AB} 8.3); ν_{max}(KBr)/cm^{-1} 1584, 1464, 1445, 1275, 1240, 1217, 1204, 1121, 1042, 1034, 1013, 762 and 681; *m/z* 693 (Ar_4Bi), 451 (Ar_2Bi), 330 (ArBi) and 209 (Bi) (Found: C, 54.07; H, 5.01. $C_{39}H_{43}Bi\ O_7S$ requires C, 54.17; H, 5.01 %).

Tetrakis-(2-methoxyphenyl)bismuthonium bromide monohydrate 7a. To a solution of compound **3a** (235 mg, 0.34 mmol) in methylene dichloride (10 cm^3) was added an aqueous solution (10 cm^3) of sodium bromide (2 g) and the resulting mixture was stirred vigorously

for 30 min at room temperature. Usual work up gave compound **7a** (184 mg, 74 %) as fine colourless crystals. Mp 220-223 °C (dec.); δ_H 1.67 (2 H, br s), 3.67 (12 H, s), 7.22~7.32 (8 H, m) and 7.55~7.75 (8 H, m); δ_C 56.66, 112.75, 124.63, 127.36 (Bi-C), 134.31, 134.92 and 159.87; ν_{max}(KBr)/cm^{-1} 3450 (br), 1470, 1435, 1277, 1244, 1044, 781 and 760; (Found: C, 46.00; H, 3.93. $C_{28}H_{30}BiBrO_5$ requires C, 45.71; H, 4.08 %).

Tetrakis-(2-methoxyphenyl)bismuthonium iodide monohydrate 8a. Similarly obtained from compound **3a** (235 mg, 0.34 mmol) and sodium iodide (2 g). Yield, (198 mg, 74 %). Mp 202-204 °C (dec.); δ_H 1.61 (2 H, br s), 3.67 (12 H, s), 7.22~7.32 (8 H, m) and 7.55~7.75 (8 H, m); δ_C 56.76, 112.76, 124.66, 127.33 (Bi-C), 134.30, 134.92 and 159.84; ν_{max}(KBr)/cm^{-1} 3450 (br), 1470, 1435, 1277, 1244, 1044, 781 and 760; (Found: C, 42.73; H, 3.72. $C_{28}H_{30}BiIO_5$ requires C, 42.97; H, 3.84 %).

Oxidation of bismuthane 1a with iodosylbenzene

In benzene in the presence of alkyl halides: typical procedure. A mixture of bismuthane **1a** (530 mg, 1 mmol), iodosylbenzene (330 mg, 1.5 mmol), benzyl bromide (1 mmol, 171 mg), and benzene (50 cm^3) was stirred at 40~50 °C for 5 h. The resulting suspension was filtered through a Celite bed and the filtrate was evaporated to give an oily residue (597 mg), which was passed through a short column of silica gel to give an oily mixture (278 mg), the composition of which was estimated by ^{1}H-NMR analysis as follows; bismuthane **1a** (0.09 mmol), anisol (0.09 mmol), benzyl bromide (0.74 mmol) iodobenzene (0.45 mmol), and benzaldehyde (0.02 mmol). The solid residue on a Celite bed was extracted with methylene dichloride (20 cm^3

x 4) and the combined extracts were evaporated off to give bismuthonium salt **7a** (309 mg, 42 %). Similar oxidation of bismuthane **1a** in the presence of ethyl bromide and 2,2,2-trifluoroethyl iodide gave the corresponding bismuthonium bromide **7a** and iodide **8a** in 39 % and 13 % yields, respectively.

Preparation of tetrakis-(4-methoxyphenyl)bismuthonium tertafluoroborate 11b

To a solution of 4-methoxyphenylmagnesium bromide, prepared from 4-bromoanisole (1.12 g, 6 mmol) and magnesium (0.146 g, 6 mmol) in THF (7 cm^3), was added dropweise a solution of tris-(4-methoxyphenyl)bismuth dichloride **5b**[28] (1.46 g, 2.43 mmol) in THF (10 cm^3) at -60 °C, and the reddish purple suspension was allowed to warm to room temperature. The mixture was stirred at the same temperature for 30 min, and treated with a mixture of trimethylsilyl trifluoromethanesulfonate (0.70 cm^3, 3.5 mmol) and ethanol (0.25 cm^3) in THF (5 cm^3) at -40 °C. The characteristic purple colour of pentaarylbismuth faded out completely, and the resulting pale yellow solution was stirred at room temperature for 30 min, and contentrated to dryness. The residue was dissolved in CH_2Cl_2 (15 cm^3) and stirred vigorously with an aueous solution (30 cm^3) of sodium tetrafluoroborate (3 g) for 2 h at room temperature. Organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (5 cm^3 x 3). The combined organic phase was dried ($MgSO_4$) and evaporated to afford a yellow oily residue, which was chlomatographed on silica-gel using CH_2Cl_2. The onium salt **11b** was obtained in 67% yield (1.19 g) as a colourless crystals. *Compound*

11b; mp 174-175 °C; δ_H 3.85 (12 H, s), 7.20 (8 H, d, J_{AB} 8.8) and 7.65 (8 H, d, J_{AB} 8.1); δ_C 55.5 (MeO-), 118.0, 125.1 (Bi-C), 136.8 and 162.7; ν_{max}(KBr)/cm^{-1} 1580, 1568, 1489, 1458, 1296, 1254, 1179, 1121, 1050, 1017, 822, 521 and 513 (Found: C, 46.64; H, 3.85. $C_{28}H_{28}BiBF_4O_4$ requires C, 46.43; H, 3.90%).

Treatment of salt **11b** (0.362 g, 0.5 mmol) with an excess of brine in CH_2Cl_2 at room temperature readily gave bismuthane **1b** and 4-chloroanisole quantitatively. After recrystallization from CH_2Cl_2-EtOH, 0.252 g (95%) of bismuthane **1b** was obtained.

Metathesis reaction of tris-(2-methoxyphenyl)bismuth dichloride 5a with silver(I) perchlorate

In acetone. To a solution of **5a** in acetone (50 cm^3) was added commercial silver(I) perchlorate (460 mg, 2 mmol; from Wako Pure Chemical Industries. LTD. content 90 %) in the same solvent (10 cm^3) and the resulting suspension was stirred at room temperature in the dark. After 1 h the precipitated silver chloride was filtered off and the filtrate was concentrated under reduced pressure to leave a dark brown oily residue, which was triturated with a mixture of acetone (2 cm^3) and benzene (20 cm^3) to give a tris-(2-methoxyphenyl)(2-oxopropyl)bismuthonium perchlorate **14a** as light brown crystals (375 mg, 55 %). *Compound* **14a**, mp 149-150 °C (dec.); δ_H 2.48 (3 H, s), 3.82 (9 H, s), 5.09 (2 H, s), 7.15~7.30 (6 H, m) and 7.50~7.65 (6 H, m); δ_C 30.28, 51.79, 56.54 (Bi-CH_2), 112.19, 124.34, 126.23 (Bi-C), 134.07, 135.14, 159.97 and 202.99 (C=O); ν_{max}(KBr)/cm^{-1} 1458, 1429, 1233, 1092, 1049, 1021 and 758 (Found: C, 41.96; H, 3.77. $C_{24}H_{26}BiClO_8$ requires C, 41.97; H, 3.82 %).

Treatment of salt **14a** with an excess of brine in chloroform at room temperature readily gave bismuthane **1a** quantitatively.

In butan-2-one. Dichloride **5a** in butan-2-one (50 cm^3) was treated with silver(I) perchlorate (460 mg, 2 mmol, from Wako Pure Chemical Industries. LTD., content 90 %). Usual work up gave a dark brown oily residue, which was triturated with a mixture of MeOH (2 cm^3) and EtOAc (20 cm^3) to give tetrakis-(2-methoxyphenyl)bismuthonium perchlorate **13a** as light brown crystals (8 mg, 1 %), mp 250-251 °C; δ_H 3.66 (12 H, s), 7.25~7.35 (8 H, m) and 7.55~7.75 (8 H, m); δ_C 56.39, 112.58, 124.51, 127.19 (Bi-C), 134.20, 134.86 and 159.79; ν_{max}(KBr)/cm^{-1} 1472, 1435, 1279, 1244, 1098, 1044 and 762 *m/z* 637 (Ar_4Bi), 423 (Ar_2Bi), 316 (ArBi) and 209 (Bi) (Found: C, 45.67; H, 3.80. $C_{28}H_{28}BiClO_8$ requires C, 45.62; H, 3.80 %).

Reaction of dichloride 5a with silver(I) oxide in methylene dichloride. To a suspension of silver(I) oxide, freshly prepared from 4 mmol of silver(I) nitrate and sodium hydroxide in methylene dichloride (5 cm^3), was added dichloride **5a** (601 mg, 1 mmol) in the same solvent (45 cm^3) and the resulting suspension was heated at reflux in the dark. After 4 h, the mixture was filtered through a Celite bed and the filtrate was evaporated off under reduced pressure to leave a light yellow solid, which contained tetrakis-(2-methoxyphenyl)bismuthonium hydroxide trihidrate **15a** and bismuthane **1a**. The presence of a formate in the product mixture was detected by ^{1}H-NMR spectroscopy. The mixture was recrystallized from CH_2Cl_2-EtOAc (1 : 5) to deposit compound **15a** (271 mg, 38 % based on Bi). *Compound* **15a**, mp 155~160 °C (dec.); δ_H 2.77 (6 H, br s), 3.67 (12 H, s), 7.22~7.32 (8 H, m)

and 7.55~7.75 (8 H, m), OH group was not observed; ν_{max}(KBr)/cm^{-1} 3450 (br), 1586, 1566, 1471, 1277, 1244, 1044, 1009, 783 and 760 (Found: C, 47.53; H, 4.60. $C_{28}H_{35}BiO_8$ requires C, 47.46; H, 4.94 %). Compound **15a** was also obtained by the reaction of salt **3a** and silver (I) oxide as follows; to a suspension of salt **3a** in THF (30 cm^3) {prepared from bismuthane **1a** (1 mmol, 530 mg) and iodosylbenzene (2 mmol, 440 mg)}, was added silver(I) oxide (prepared from silver nitrate 1.1 mmol and sodium hydroxide) in water (5 cm^3) and the resulting suspension was stirred for 40 min in the dark under ambient conditions. Organic solvent was removed under reduced pressure and the aqueous layer was extracted with methylene dichloride (20 cm^3 x 4). The combined extracts were dried ($MgSO_4$) and evaporated off under reduced pressure to leave compound **15a** (392 mg, 55 %).

Treatment of compound **15a** with 42 % tetrafluoroboric acid in acetonitrile at 0~5 °C gave the correspomding tetrafluoroborate **11a** (mp 268 ~270 °C) in 91 % yield.

Oxidation in the presence of a radical scavenger

A mixture of bismuthane **1a** (530 mg, 1 mmol), iodosylbenzene (286 mg, 1.3 mmol), 1,1-diphenylethylene (2 mmol, 360 mg) and methylene dichloride (50 cm^3) was heated to reflux, and after 1.5 h it was filtered through a Celite bed. Usual workup gave the salt **3a** (299 mg, 43 %). 1,1-Diphenylethylene was recovered unchanged from the mother liquor, from which the salt **3a** had separated out.

Crossing over between bismuthanes 1a and 1d during the

oxidation with iodosylbenzene

A mixture of bismuthanes **1a** (265 mg, 0.5 mmol), **1e** (286 mg, 0.5 mmol), iodosylbenzene (330 mg, 1.5 mmol) and methylene dichloride (50 cm^3) was heated to reflux for 1 h. Usual workup gave a mixture of bismuthonium salts (284 mg), which was found by FAB-MS analysis to contain **3a**, **3e**, tris-(2-methoxyphenyl)(2-methoxy-4-methylphenyl) and (2-methoxyphenyl)tris-(2-methoxy-4-methylphenyl)-bismuthonium chlorides; *m/z*; 693 (Ar^1_4Bi), 679 ($Ar^1_3Ar^2Bi$), 651 ($Ar^1Ar^2_3Bi$), 637 (Ar^2_4Bi), 451 (Ar^1_2Bi), 437 (Ar^1Ar^2Bi), 423 (Ar^2_2Bi), 330 (Ar^1Bi), 316 (Ar^2Bi), and 209 (Bi) (^1Ar = 2-methoxy-4-methylphenyl, ^2Ar = 2-methoxyphenyl).

Attempt to prepare μ-oxybis{tris-(2-methoxyphenyl)bismuth} di(trifluoromethanesulfonate)

To a suspension of dichloride **5a** (601 mg, 1 mmol) in dry methylene dichloride (8 cm^3), was added trimethylsilyl trifrate (0.19 cm^3, 1 mmol) at 0 °C, and the mixture was stirred at room temperature for 20 h. To the resulting yellow solution, was added hexamethyldisiloxane (0.11 cm^3, 0.5 mmol) and stirred for 48 h at room temperature to give a brown solution, which was evaporated under reduced pressure to obtain a grey solid (680 mg). ^1H-NMR spectrum of the mixture supported that the mixture contained at least four products, including bismuthonium salt. The starting material **5a** was found to be consumed completely. The residue was dissolved in methylene dichloride (15 cm^3) and shaked with brine vigorously for 3h. After extractive work up, a dark brown solid (245 mg) was obtained. The residue was chromatographed on silica gel using

methylene dichloride-ethanol (1 : 0 ~ 10 : 1) to give dichloride **5a** (68 mg, 11%) and bismuthonium salt **3a** (113 mg, 16%).

X-Ray crystallography of compound 7a

A crystal of dimensions 0.450 X 0.380 X 0.200 mm, grown from a mixture of EtOH-EtOAc (1 : 5) at room temperature, was sealed in a glass capillary and used for X-ray crystallography.

Crystal data. $C_{28}H_{28}O_4BiBr$, M = 717.41. Monoclinic. Space group $P2_1/c$, $a = 11.466(4)$ Å, $b = 19.802(9)$ Å, $c = 12.369(5)$ Å, $\beta = 103.30(3)°$, $V = 2733(2)$ Å^3, $Z = 4$, $D_c = 1.743$ g/cm^3. Prisms, μ(Mo-Kα, λ = 0.71069 Å) = 79.08 cm^{-1}.

Data collection and processing. Intensity data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo-Kα radiation from a 12 KW rotating anode generator using the ω-2θ scan technique to a maximum 2θ value of 55.0°. Scans of (0.79 + 0.30 tan θ)° were made at a speed of 16.0 deg min^{-1} (in omega). Data were corrected for Lorentz and polarization effects. Of the 6754 reflections which were collected, 6446 were unique (R_{int} = 0.074). The intensities of three representative reflections which were measured after every 150 reflections declined by 5.7%. A linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction, based on azimuthal (Ψ) scans of several reflections, was applied which resulted in transmission factors ranging from 0.53 to 1.00.

Structure analysis and refinement. The structure was solved by direct methods. The non-hydrogen atoms were refined

anisotropically. The positions of hydrogen atoms were calculated from those of the non-hydrogen atoms and were included in the F_c calculation. The final cycle of full-matrix least-squares refinement, $\Sigma w(|F_0| - |F_c|)^2$ where: $w = 1/\sigma^2(F_0)$, was based on 3547 observed reflections [$I > 2.50\sigma(I)$] and 308 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.042$ and $R_w = 0.036$. The weighting scheme, $w = 1/\sigma^2(F_0)$, was employed. The standard deviation of an observation of unit weight was 1.17,† and the maximum peak and minimum though in the final DF syntheses surpluses which are 0.80 and -1.34 $Å^{-3}$. All calculations were performed using the TEXSAN[29] crystallographic software package of the Molecular Structure Corporation. The ORTEP[30] program was used to obtain the drawing in Fig.1. Selected bond lengths and bond angles, and fractional atomic coordinate are given in Table 2. §

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Footnotes

† One referee suggested the possibility of direct formation of benzaldehyde from the adduct of type **16** formed from benzyl bromide and the corresponding bismuthane oxide.

‡ Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1, 1996*, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/109.

§ Standard deviation of an observation of unit weight: $[\Sigma w(|F_0| - |F_c|)^2/(N_0-N_v)]^{1/2}$ where N_0 = number of observations and N_v = number of variables.

Chapter 3 A Convenient in situ Generation and Mild Oxidizing Ability of Triarylbismuthane Tosylimides

Abstract

Direct imination of triarylbismuthanes **1** with (tosyliminoiodo)benzene **2** to triarylbismthane *N*-tosylimide **3** was performed under mild conditions. The bismuthane imides **3** were found to posess a mild oxidizing ability to convert activated alcohols into the correspomding carbonyl compounds. Tris-(4-methylphenyl)stibane **4** is similarly iminated to give the stibane imide **5**, which lacks the corresponding oxidizing ability.

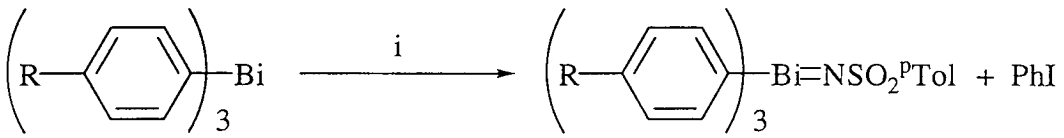
Introduction

The chemistry of triorganylbismuth imines has not been studied much. Wittig *et al.* reported in 1964 the first synthesis of triphenylbismuthane *N*-tosylimide (**3a**) by the direct action of anhydrous Chloramine-T on bismuthane **1a** in boiling acetonitrile.[1] We also prepared several bismuthane imides according to Wittig's procedure and examined their chemistry in some detail. Bismuthane imides **3a** and **3b** reacted with aromatic aldehydes, benzoyl chloride and phenyl isocyanate to give *N*-arylidene-toluene-*p*-sulfonamides, *N*-benzoyl-toluene-*p*-sulfonamide and *N*-aryl-*N'*-tosylureas, respectively.[2] Both groups failed to isolate the bismuthane imides as crystals due to moisture sensitivity. Recently, Naumann *et al.* were successful in obtaining several bismuthane imides as crystalline solids by treatment of triarylbismuth difluorides with *N*, *N*-

bis(trimethylsilyl)sulfonamides.[3] They reported that the bismuthane imide **3a** underwent gradual hydrolysis in wet dioxane to give triphenylbismuthane oxide and toluene-*p*-sulfonamide in almost quantitative yields. However, both methods for the preparation of the bismuthane imides **3** are not free from drawbacks; Wittig's method uses dehydrated Chloramine-T as oxidant, which is potentially explosive and troublesome to prepare, while Naumann's method requires a multi-step procedure for the preparation of starting materials.

Results and Discussion

We have found that (tosyliminoiodo)benzene(**2**)[4] smoothly transfers its imino function to triarylbismuthanes **1** under mild conditions to form triarylbismuthane tosylimides **3** almost quantitatively. Thus, when a suspension of an equimolar amount of bismuthane **1** and (tosyliminoiodo)benzene **2** in dry dichloromethane was stirred for 0.5 h at ambient temperature, there resulted a clear yellow solution of bismuthane imide **3** (Scheme 1).



1a, b **3a, b**

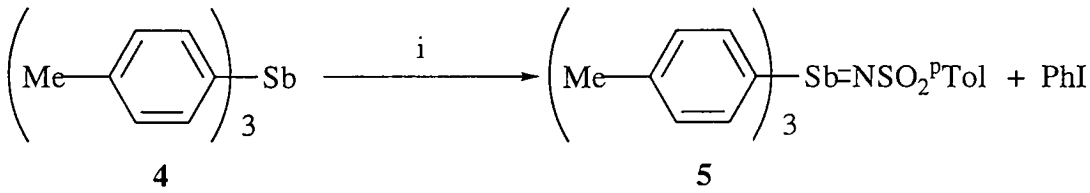
Scheme 1

Reagent and conditons: i, PhI=$NSO_2{}^pTol$ **2**, CH_2Cl_2, r.t.

A trapping experiment of bismuthane imide **3a** with acetic acid gave a mixture of the expected triphenylbismuth diacetate,[5] iodobenzene and

toluene-*p*-sulfonamide in stoichiometric yield, confirming that bismuthane imide **3 a** was formed quantitatively by the present procedure.

This imination procedure proved to be useful also for the *in situ* preparation of triarylstibane imines.[1,6] (Iminoiodo)benzene **2** reacted rapidly with tris(4-methylphenyl)stibane **4** under similar conditions to give the corresponding triarylstibane imide **5** almost quantitatively as a colourless solution (Scheme 2).



4 **5**

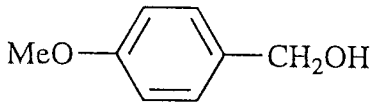
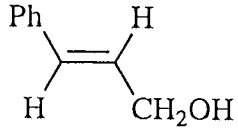
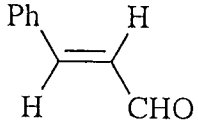
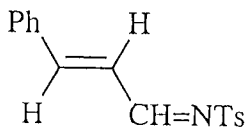
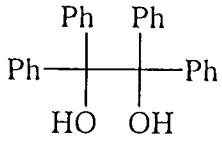
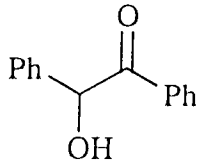
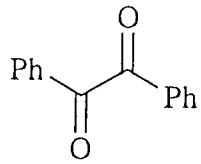
Scheme 2

Reagent and conditons: i, PhI=$NSO_2{}^{p}$Tol **2**, CH_2Cl_2, r.t.

We have recently reported a mild oxidizing ability of triarylbismuthane oxides toward alcohols.[7] As part of our study on the oxidation with bismuth(V) compounds, we have now examined the reaction of bismuthane imides **3** with a series of alcohols. Treatment of tris(4-methylphenyl)bismuthane imide **3b** with alcohols as well as benzoin were easily oxidized to the corresponding carbonyl compounds, while benzopinacol was cleaved to benzophenone. However, primary alcohols were not oxidized (Table 1). The reaction proceeded smoothly at ambient temperature under neutral conditions. In the oxidation of allylic and benzylic alcohols, *N*-allylidene- and benzylidene-toluene-*p*-sulfonamides were obtained in low yields, suggesting that bismuthane imide **3b** reacted further with the resulting aldehydes *via* the Wittig-type mechanism.

Table 1. Oxidation of Alcohols with Bismuthane Imide **3b**

$$^{p}Tol_3Bi + PhI{=}NSO_2{}^{p}Tol \xrightarrow{-\,PhI} {}^{p}Tol_3Bi{=}NSO_2{}^{p}Tol \xrightarrow[r.t.]{ROH}$$

ROH	Products				
$PhCH_2CH_2OH$	$^{p}Tol_3Bi$ 73%	$TsNH_2$ 81 %	($PhCH_2CH_2OH$ 100 %)		
	$^{p}Tol_3Bi$ 35%	$^{p}AnCHO$ 63 %	$^{p}AnCH{=}NTs$ 21 %	$TsNH_2$ 35 %	$^{p}Tol_2BiNHTs$ 43 %
	$^{p}Tol_3Bi$ 9%	 70 %	 18 %	$TsNH_2$ 47 %	$^{p}Tol_2BiNHTs$ 39 %
	$^{p}Tol_3Bi$ 99%	$Ph_2C{=}O$ 99 %	$TsNH_2$ 83 %		
	$^{p}Tol_3Bi$ 72%	 54 %	PhCHO 13 %	$TsNH_2$ 90 %	

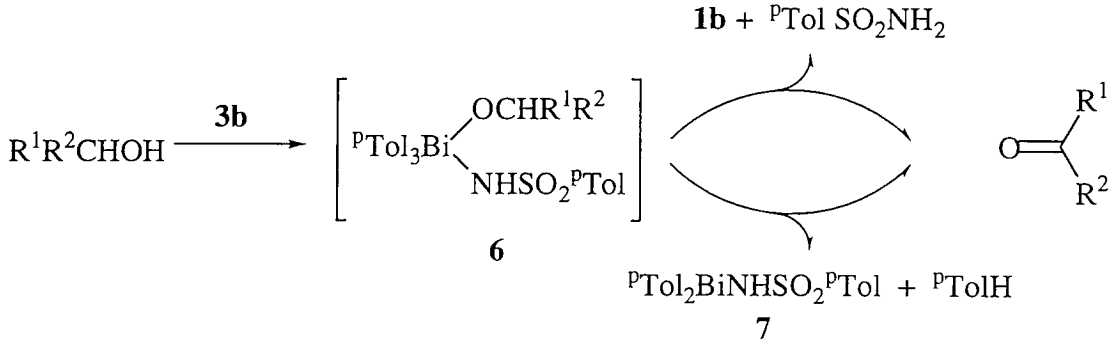
The most striling result was the isolation of bis(p-methylphenyl)bismuthyl *N*-tosylamide **7** in moderately yields in the case of the oxidation of allylic and benzylic alcohols. The amide was easily removed off from ther eaction mixture only extracting with benzene due to its low solubility in cold benzene. It seems to be insensitive against atmospheric moisture in the solid state, however, it slowly decomposes to tris-(4-methylphenyl)bismuthane **1b** and insoluble white powder in solution.

An additional important result of the present work was the first isolation of a stable aminobismuthane derivative, bis(4-methylphenyl)(tosylamino)bismuthane (**7**). The amine **7** was obtained in moderate yield from the reaction of allyic or benzylic alcohols with compound **3b**. When the solid residue obtained after evaporation of the reaction mixture unde reduced pressure was repeatedly washed with cold benzene to remove any soluble organic substances, compound **7** remained as a difficulty soluble white powder, which was not so sensitive toward atmospheric moisture in a solid state, but slowly decomposed to bismuthane **1b** and a white powderly deposit when stood in $CDCl_3$.

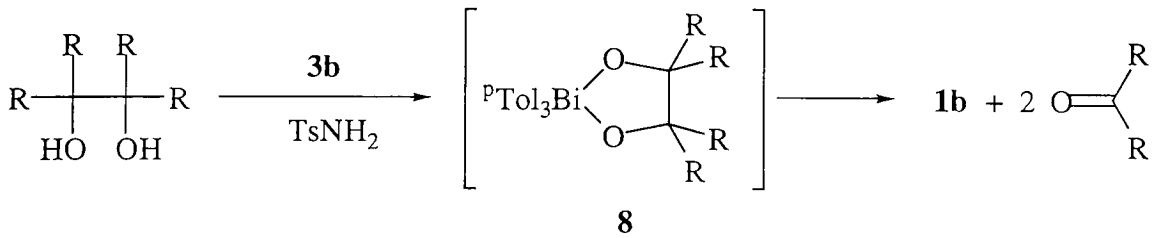
The formation of aminobismthane derivative **7** suggests that the oxidation of alcohols by compound **3** may proceed via two different pathways. In one pathway, the -NHTs group and an α-proton of the alkoxy function are simultaneously eliminated from the adduct **6** to form the corresponding carbonyl compound, bismuthane and toluene-*p*-sulfonamide, while in the other pathway the -Ar group and the α-proton combine to yield the

aminobismuthane **7** and a carbonyl compound (Scheme 3). In the case of primary alcohols, however, both modes of degradation would become more difficult for the pentavalent intermediate **6**; 2-phenylethanol disappeared rapidly when treated with bismuthane imide **3b** (checked by TLC), but subsequent reaction did not apparently proceed. Heating of the reaction mixture at reflux only resulted in the regeneration of the original alcohol accompanied by bismuthane **1b**. On the other hand, the oxidation of benzopinacol with compound **3b** gave benzophenone and bismuthane **1b** in quantitative yields, suggesting a possible intermediacy of a five-membered ring (**8**). Tertiary alcohols seem to be inert toward bismuthane imide **3b**; quenching of the reaction mixture of α-terpineol and **3b** with acetic acid gave the unchanged alcohol, tris-(4-methylphenyl)bismuth diacetate[5] and toluene-*p*-sulfonamide in stoichiometric yield.

2°, Allylic, Benzylic Alcohols



Diols



Scheme 3

In order to compare the oxidizing ability of stibane imides and bismuthane imides, stibane imide **5** was treated with several alcohols, listed in Table 1. Similarly to triphenylstibane oxide[8], compound **5** exhibited only limited oxidizing ability toward organic substrates; stirring of an equimolar mixture of imide **5** and a given alcohol in dichloromethane at ambient temperature under argon resulted in most cases in consume of starting materials, but the expected oxidation products were not obtained. The only exceptions were benzoin and benzopinacol, which were oxidized to benzil and benzophenone, respectively, just as had been observed in the reaction with triphenylstibane oxide. These results also clearly show the different chemical nature of the formal "Bi=NR" bond from the Sb=NR bond.[1,6b,9] A similar difference in chemical reactivity was also observed between the formal "Bi=O" bond and the other pnicogen-oxygen double bonds (P=O, As=O and Sb=O).

Experimental Part

Mps were determined on a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra were recorded as KBr pellet on a Shimadzu FTIR-8100 spectrophotometer. ^{1}H NMR spectra were recorded in CDCl3 on a Varian Gemini-200 (200 Mhz) spectrometer with Me4Si as an internal standard. Mass spectra (FAB) were determined on a JEOL JMS HS 110 mass spectromete, using 3-nitrobenzyl alcohol as matrix. Microanalysis was performed at Microanalytical Laboratory, Institute of Chemical Research, Kyoto University.

Typical Procedure for *in situ* Generation of Triarylbismuthane Tosylimide

A suspension of triphenylbismuthane **1a** (440 mg, 1.0 mmol) and (tosyliminoiodo)benzene **2** (373 mg, 1.0 mmol) in dry dichloromethane (30 cm^3) was stirred at ambient temperature under argon until it became clear yellow. Bismuthane **1a** was completely consumed at this stage (checked by TLC; if part of bismuthane **1a** remains unchanged after disappearance of iminnoiodo compound **2**, add further amounts of the imination reagent). It usually took 0.5 h to complete the reaction. The resulting yellow solution of bismuthane imide **3a** was used as such for the further experiments. Evaporation of the solution under reduced pressure gave a mixture of imide **3a** and iodobenzene as a bright yellow syrup. Since compound **3a** is known, no attempt was made to isolate it.

Typical Procedure for *in situ* Generation of Triarylstibane Tosylimide

A suspension of tris(4-methyphenyl)stibane **4** (394 mg, 1.0 mmol) and iminoiodobenzene **2** (373 mg, 1.0 mmol) in dichloromethane (30 cm^3) was stirred at ambient tempereture under argon. The reaction completes within 5 min and tris(4-methylphenyl)stibane tosylimide **5** was obtained as a colourless solution. On treatment with water under aerial conditions, this solution afforded tris(4-methylphenyl)stibane oxide and toluene-*p*-sulfonamide in quantitative yields.

Trapping Experiment of Bismuthane Imide

A solution of riphenylbismuthane *N*-tosylimide **3a**, prepared from triphenylbismuthane **1a** (220 mg, 0.5 mmol) and (iminoiodo)benzene **2** (224 mg, 0.6 mmol) was treated with acetic acid (78 mg, 1.3 mmol) at ambient temperature, and the resuting mixture was stirred for 1 h. The mixture was evaporated to leave an orange coloured solid (391 mg), which contained triphenylbismuth diacetate[5] and toluene-*p*-sulfonamide in the ratio of 1:1.2 (estimated by ^{1}H NMR), suggesting that their yield were quantitative.

General Procedure for the Oxidation of activated Alcohols with Triarylbismuthane Imide

To an in situ prepared solution of bismuthane imide **3b** (1 mmol) in dichloromethane (30 cm^3) was added an alcohol (1 mmol) and the resulting mixture was stirred at ambient temperature for 10 h. After completion of the reaction the mixture was evaporated under reduced pressure to leave a solid residue, which was triturated with benzene (15 cm^3) and filtered through a thin Celite bed. The residue was washed with benzene (5 cm^3 x 2) and the washings were combined with filtrate. The solvent was removed under reduced pressure and the residue was chromatographed on silica-gel using hexane-ethyl acetate (1:0 – 1:2) as an eluent.

Cinnamil alcohol. Treatment of cinnamil alcohol (134 mg, 1 mmol) with 1.0 mmol of bismuthane imide **3b** prepared from 1.0 mmol of bismuthane **1b** and 1.2 mmol of **2** gave bismuthane **1b** (45 mg, 9%), cinnamaldehyde (93 mg, 70%), *N*-(toluene-*p*-sulfonyl)-cinnamaldehyde

imine[10] (62 mg, 22%) and toluene-*p*-sulfonamide (89 mg, 47%) after column chromatography. The residue on the Celite bed was extracted with chloroform (5 cm^3 x 6) and the combined extracts were evaporated to give bis-(4-methylphenyl){*p*-toluenesulfonyl)amino}bismuthane (**7**) as a colourless microcrystalline solid (278 mg, 39%). Compound **7**, mp 163-165 °C; δ_H 2.34 (6 H, s), 2.38 (3 H, s), 4.33 (1 H, br s), 7.16 (2 H, br d, J=8), 7.40 (4 H, d, J_{AB} = 8.0), 7.62 (2 H, br d, J = 8) and 7.88 (4 H, d, J_{AB} = 8.0); νmax/cm^{-1} (KBr) 3281, 1487, 1312, 1294, 1279, 1134, 1086, 947, 928, 808, 793, 668, 563, 544 and 478; *m/z* (FAB) 952 {$(Tol_2Bi)_2NHTs$}, 861 ($Tol_2BiNHTsBiTol$), 707{$(Tol_2Bi)_2NH_2$}, 562 (Tol_2BiNH_2Ts), 544 {$Tol_2BiNS(O)Tol$}, 470 (TolBiNHTs), 391 (Tol_2Bi) and 300 (TolBi). (Found: C, 44.6; H, 3.9; N, 2.6. $C_{21}H_{22}BiNO_2S$ requires C, 44.92; H, 3.95; N, 2.49%).

4-Methoxybenzyl alcohol. Treatment of 4-methoxybenzyl alcohol (69 mg, 0.5 mmol) with 0.5 mmol of bismuthane imide **3b** prepared from 0.5 mmol of bismuthane **1b** and 0.6 mmol of **2**, gave bismuthane **1b** (85 mg, 35%), 4-methoxybenzaldehyde (43 mg, 63%), *N*-(toluene-*p*-sulfonyl)-4-methoxybenzaldehyde imine[8] (31 mg, 21%) and toluene-*p*-sulfonamide (33 mg, 35%) after column chromatography. By the same procedure, compound **7** was obtained in 43% (121 mg).

Benzopinacol. Treatment of benzopinacol (183 mg, 0.5 mmol) with 0.5 mmol of bismuthane imide **3b**, prepared from 0.5 mmol of bismuthane **1b** and 0.6 mmol of **2**, gave bismuthane **1b** (237 mg, 99%), benzophenone (180 mg, 99%) and toluene-*p*-sulfonamide (85 mg, 83%) after column chromatography.

Benzoin. Treatment of benzoin (106 mg, 0.5 mmol) with 0.5 mmol of bismuthane imide **3b**, prepared from 0.5 mmol of bismuthane **1b** and 0.5 mmol of **2**, gave bismuthane **1b** (173 mg, 72%), oxidized products (88 mg) and toluene-*p*-sulfonamide (77 mg, 90%) after column chromatography. The components of oxidized products were unchanged benzoin (20%), benzaldehyde (13%) and benzil (54%). The yield of these compounds was estimated by ^{1}H NMR.

4-*tert*-Butyl-cyclohexanol. Treatment of 4-*tert*-butyl-cyclohexanol (153 mg, 1.0 mmol) with 1.0 mmol of bismuthane imide **3b**, prepared from 1.0 mmol of bismuthane **1b** and 1.1 mmol of **2**, gave bismuthane **1b** (111 mg, 23%) and a mixture (223 mg) after column chromatography. The components of a mixture were iodobenzene (17%) unchanged alcohol (33%), 4-*tert*-butyl-cyclohexanone (52%) and toluene-*p*-sulfonamide (47%). The yield of these compounds was estimated by ^{1}H NMR. In addition, compound **7** was obtained in 47% (262 mg).

2-Phenylethanol. Treatment of 2-phenylethanol (112 mg, 1.0 mmol) with 1.0 mmol of bismuthane imide **3b**, prepared from 1.0 mmol of bismuthane **1b** and 1.0 mmol of **2** led to complete consumption of the starting alcohol (checked by TLC) after 3 h. The reaction mixture was heated at reflux for 5 h, and concentrated to leave a yellow solid, which was chromatographed to afford bismuthane **1b** (351 mg, 73%) and a mixture (265 mg) of 2-phenylethanol (100%) and toluene-*p*-sulfonamide (81%). The yield was estimated by ^{1}H NMR.

α-Terpineol. α-Terpineol (77 mg, 0.5 mmol) was treated with 0.5 mmol of bismuthane imide **3b**, prepared from 0.5 mmol of bismuthane **1b** and 0.5 mmol of **2**, at ambient temperature for 19 h and the mixture was concentrated. According to ^{1}H NMR spectrum of the mixture, the starting alchohol was recovered completely. The reaction mixture was treated with acetic acid (120 mg, 2 mmol) and concentrated to leave a mixture (404 mg), which contained α-terpineol (100%), tris-(4-methylphenyl)bismuth diacetate[5] (100%) and toluene-*p*-sulfonamide (100%). The yield was estimated by ^{1}H NMR.

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Chapter 4 Preparation and the First X-ray Structure Analysis of Highly Stabilized Triarylbismuthane Imides

Abstract

Triarylbismuthane imides which contain intramolecular coordination groups were prepared by the reaction between correponding dichlorides of azabismocine **7**, azabismepine **12** and acyclic bismuthane which contained 2-(4,4-dimethyl-oxazoline-2-yl)phenyl group **18a–c**, and trifluoromethanesulfonamide in the presence of potassium *tert* butoxide in almost quantitative yields. In contrast to all known bismuthane imides, these imides from cyclic bismuth compound, **8** and **13**, as well as imide from acyclic bismuthanes **19a–c** were found to be air– and moisture– stable, and could be handled under atmospheric conditions. They can be recrystallized easily to give crystals, which melt at relatively high temperature. The molecular structure of imide **19b** was elucidated by X–ray crystallographic analysis, where the bismuth centre possessed distorted trigonal bipyramidal structure. The nitrogen atom of the oxazoline ring and oxygen atom of the sulfonyl group coordinated to the bismuth centre. The bond length of Bi–N(imide) suggested that this imide possessed a polar Bi^{+}–N^{-} single bond rather than Bi=N double bond. IR spectra of these imides exhibited strong peaks around 610 cm^{-1}, probably due to the Bi–N absorption.

Introduction

Bismuthane imides of the general formula $R_3Bi{=}NE$ are the bismuth analog of phosphane imides $R_3P{=}NE$, which have long been known as the intermediate

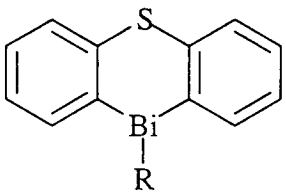
in the Staudinger reactions.[1] In contrast to those derived from lighter 15th and 16th Group elements, bismuthane imides have remained almost untouched until recently. The synthesis of bismuthane imide was first reported by Wittig and Hellwinkel in 1964, who obtained triphenylbismuthane *N*–(4–methylbenzenesulfonyl)imide **1** $Ph_3Bi{=}NSO_2pTol$ as a moisture–sensitive solid by treating triphenylbismuthane with anhydrous Chloramine–T® in boiling MeCN.[2] Reactions of this and related triarylbismuthane imides with aldehydes, acid chlorides, and isocyanates afforded the corresponding aldimines, amides and urea derivatives, respectively.[3] The reaction of triarylbismuthane with $PhI{=}NSO_2pTol$[4] is convenient for the *in situ* generation of bismuthane imides,[5] while the metathesis between triarylbismuth dihalides and sulfonamides is also efficient for the preparation of similar imides.[6] All known bismuthane imides have a sulfonyl group on the imido nitrogen atom and, though thermally stable, they are quite moisture–sensitive. Under dry nitrogen, the solid imides can be stored over weeks,[3,6] but they gradually decompose in solution. Thus, the imide **1** undergoes hydrolysis in a wet dioxane to form triphenylbismuthane oxide, $Ph_3Bi{=}O$.[6]

Results and Discussion

Heterocyclic bismuthane imides

Some heterocyclic bismuthane derivatives are known to exhibit characteristic feature; 10–alkynyl–, alkenyl– and alkyl–phenothiabismine **2** and its 5,5-dioxide **3** derivatives can be isolated as an air– and moisture stable compounds.[7] The X–ray structure analysis of 10–alkynylphenothiabismine

5,5–dioxide showed the existence of the intramolecular interaction between bismuth and oxygen, however, there seems to be no reasonable explanation on the origin of the stabilization of Bi–alkynyl, alkenyl and alkyl bond, which are generally unstable against oxidation.[8] The other methylbismuth derivatives, 6,12–dimethyl–dibenz[c,f][1,5]azabismocine **4** was reported though the chemical nature was not described in detail.[9] The chemistry of cyclic bismuthanes containing intramolecular coordination groups has been limited in the case of trivalent compound.



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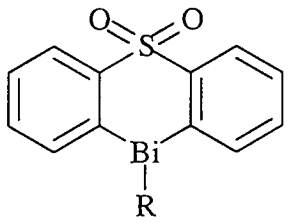

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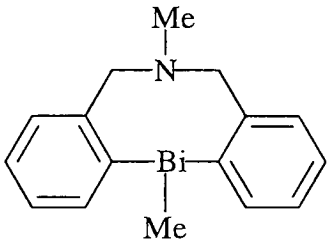
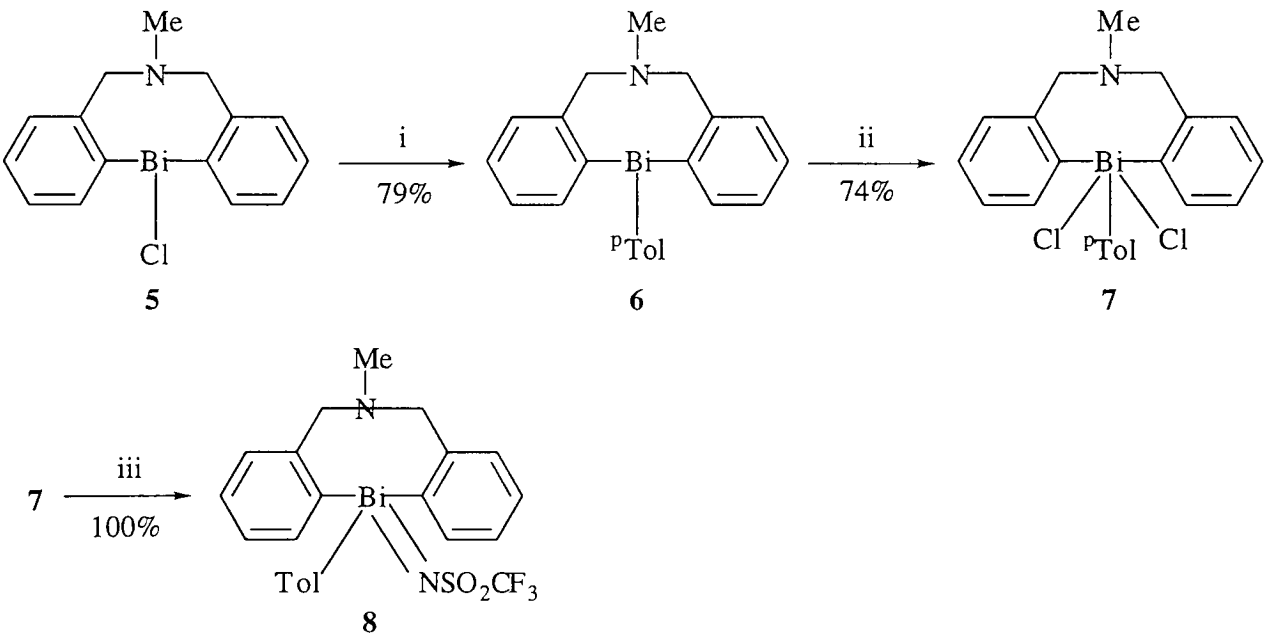


4

We tried to apply the unique chemistry of the heterocyclic bismuthane derivatives for the stabilization of bismuthane imides, pentavalent bismuth compounds, and found that the intramolecular coordination ligands was efficient to our purpose. First we tried azabismocine derivatives; 12–chloro–dibenz[c,f][1,5]azabismocine **5** was prepared in 71% yield by the modification of the reported procedure.[9] Treatment of the chlorobismuthane **5** with *p*–tolylmagnesium bromide gave the corresponding 12–(4–methylphenyl) derivative **6** in 79% yield. So the bismuthane **6** was sensitive against silica gel, it was essential to use deactivated alumina column chromatography for the purification. Then the bismuthane **6** was chlorinated with sulfuryl chloride to give the desired dichloride **7** and the chlorobismuthane **5** in 38 and 28% yield, respectively. Iodobenzene

dichloride seemed to be a more useful for our purpose; treatment of bismuthane **6** with the agent at 0–5 °C in dichloromethane afforded the dichloride **7** and the chlorobismuthane **5** in 74 and 19% yield, and they could be isolated easily by silica gel column chromatography. The dichloride **7** was thermally unstable compound, which decomposed into the chlorobismuthane **5** quantitatively when heated at 40 °C for 1 day. According to the Naumann's procedure, the dichloride **7** was treated with the mixture of $CF_3SO_2NH_2$ and $KOBu^t$ in THF at room temperature. After 1 h, the resulting suspension was evaporated to dryness, and the residue was extracted with dichloromethane successively. The combined extracts were concentrated to give the desired bismuthane imide **8** in quantitative yield (Scheme 1).



Scheme 1

Reagent and conditons: i,^{p}TolMgBr, Et_2O, 40 °C; ii, $PhICl_2$, CH_2Cl_2, 0 °–r.t.; iii, $CF_3SO_2NH_2$, $KOBu^t$, THF, r.t.

In contrast to the previously reported bismuthane imide, the imide **8** was air– and moisture–stable, and could be handled under atmospheric conditions.

By the recrystalization from benzene–acetone, it forms crystals, which melts at 177–179 °C. Elemental analysis suggested the crystal contained 2 molecule of benzene per 3 molecule of the imide. All new organobisumuth compounds **5–8** were fully characterized by ^{1}H–NMR, IR and elemental analyses. These azabismocine derivatives exhibited characteristic ^{1}H–NMR spectral features as shown in Table 1.

Table 1. Selected H-NMR spectral data of compound **5–8** (δ / ppm)

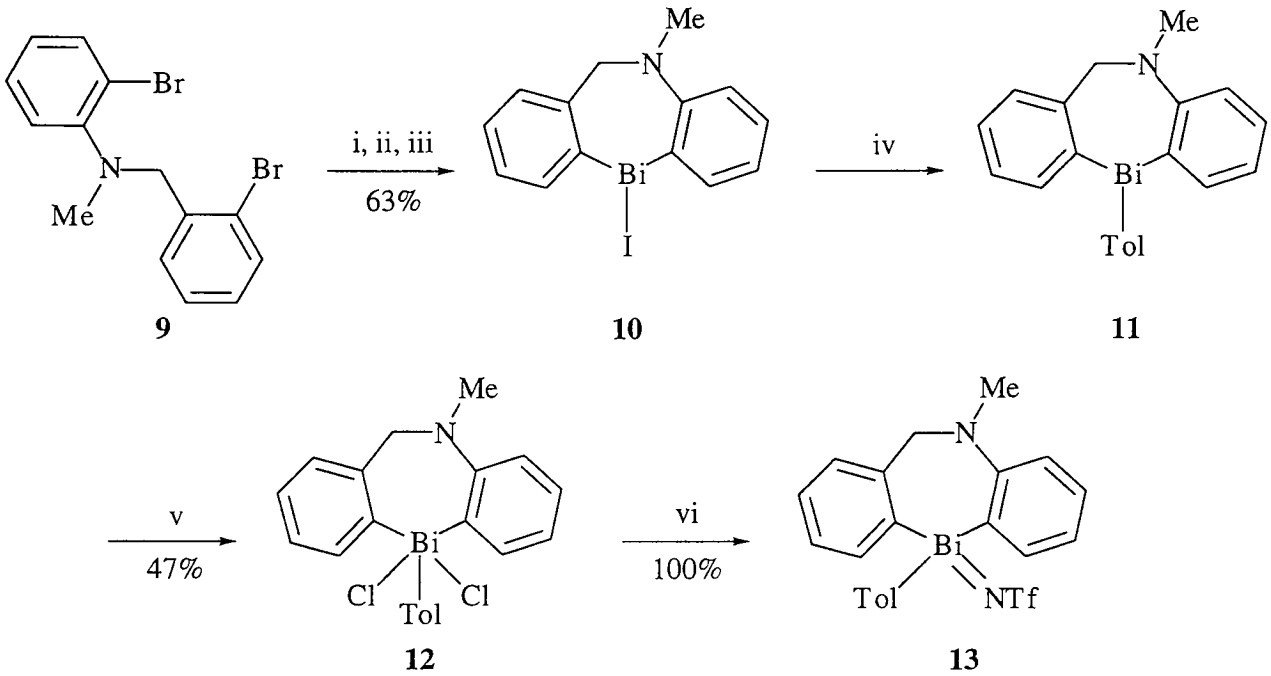
Compound	N–Me	Methylene	Aromatic proton
5	2.86	4.12, 4.27	7.30–7.60, 8.66
6	2.51	3.69, 3.93	7.05–7.59, 7.76
7	2.49	4.17, 4.75	7.40–7.75, 8.54
8	1.83	3.67, 3.90	7.25–7.70, 8.67

In a H–NMR spectrum of the imide **8**, a signal due to the *N*–Me group was observed at 1.83 ppm, which shifted to higher field with 0.68 ppm, compared with that of bismuthane **6**. Aromatic protons attached to the *ortho* positions of the bismuth center appeared at 8.67 ppm, suggesting the existence of strong interaction between the hydrogen and imide nitrogen. X–ray crystallographic study of compounds **5** and **7** have shown that these compound possess trigonal bipyramidal and octahedral structure, respectively.[10] Judging from the characteristic low field shift of the *ortho* protons, the structure of these two compounds in solution are supposed to be similar to those of the solid state.

Then the preparation of azabismepine derivatives, which contained

nitrogen and bismuth in the seven member ring, and the transformation of them to the corresponding bismuthane imides was examined. The chemistry of azaheteropines is less studied, though the preparation of azasilepine[11] and azarsepine[12] derivatives have reported. Similar to the azabismocine derivatives, dibenz[b,e][1,4]azabismepine derivatives have been prepared as follows. The amine **9** was lithiated and treated with bismuth(III) chloride in ether, and the resulting suspension was further treated with aqueous sodium iodide to give 5–methyl–11–iodo–dibenz[b,e][1,4]azabismepine **10** in 63% yield. So the iodobismuthane **10** was less soluble in ether, it separated out from the reaction mixture as orange–coloured precipitation, which was extracted with hot chloroform successively. By the action of an excess of 4–methylphenylmagnesium bromide, the iodobismuthane **10** was transformed to the corresponding triarylbismuthane **11**, which was further changed without purification, into the dichloride **12** with iodobenzene dichloride. All attempts to purify the bismuthane **11** by silica or alumina gel column chromatographies failed; the bismuthane seemed to be absorbed on such gel too strongly to be separated from them. Interestingly, the dichloride **12** could be isolated by silica gel column chromatography easily. The imination of the dichloride was carried out by the action of $CF_3SO_2NH_2$ in the presence of $KOBu^t$ in THF at room temperature, to give the desired bismuthane imide **13** in quantitative yield (Scheme 2). The imide **13** also seemed to be air– and moisture–stable compound as the imide **9**, however, the recrystallization have not been succeeded so far. Anyway, the bismuthane imide **13** prepared from

azabismepine could be handled under atmospheric conditions. The H NMR spectral feature of compound **10–13** was summarized in Table 2. Compared with those of azabismocine derivatives, the degree of the change of the chemical shifts of *N*–Me, methylene and aromatic protons are small, though compound **10**, **12** and **13** are all supposed to possess TBP structure. These phenomena would be caused by the rather rigid structure of the azabismepine derivatives.



Scheme 2

Reagent and conditons: i, BuLi, Et_2O; ii, $BiCl_3$, Et_2O, -70 °C; iii, NaI, H_2O, r.t.; iv, ^{p}TolMgBr, THF, reflux; v, $PhICl_2$, CH_2Cl_2, 0 °–r.t.; vi, $CF_3SO_2NH_2$, KOBu^{t}, THF, r.t.

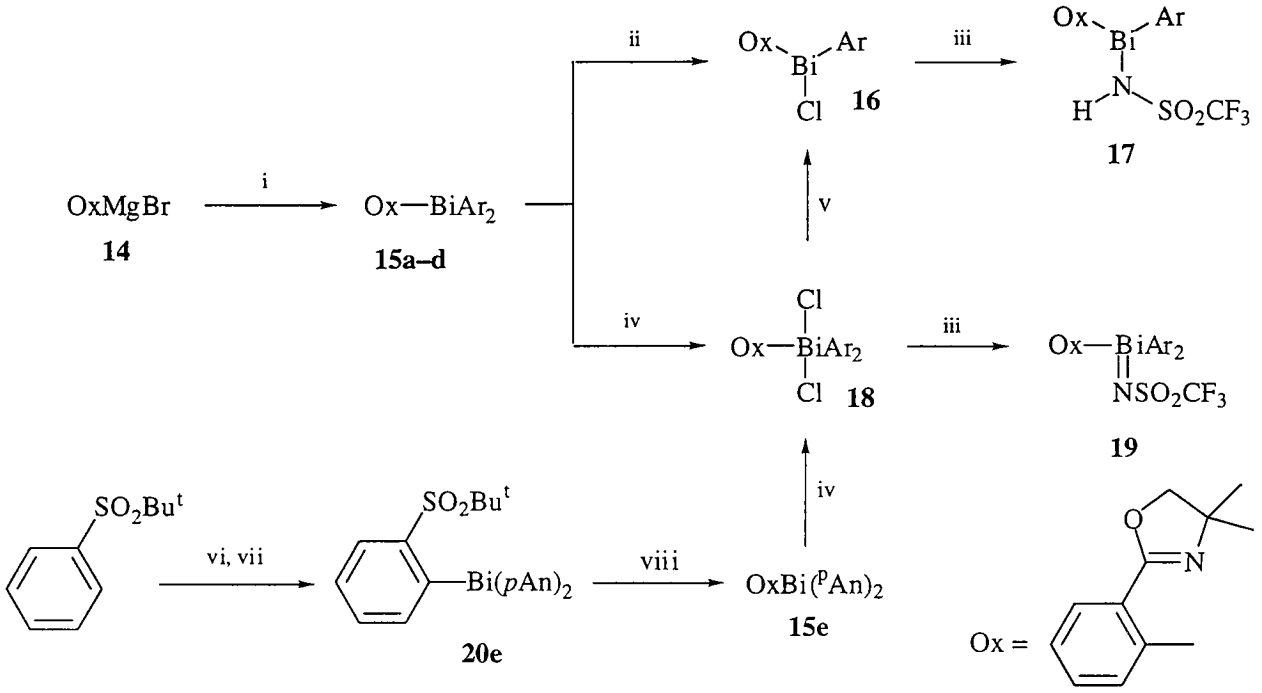
Table 2. Selected H NMR spectral data of compound **10–13** (δ / ppm)

Compound	N–Me	Methylene	Aromatic proton
10	3.14	4.40, 5.10	7.30–7.60, 8.89, 9.02
11	2.89	4.06, 4.36	6.94–7.75
12	2.91	4.16, 5.18	7.32–7.80, 8.65
13	2.71	4.28, 4.45	7.30–7.70, 8.27, 8.42

Bismthane imides containing oxazoline groups

Then we prepared a highly stabilized bismuthane imides, bearing an oxazoline group as the protecting ligand at *ortho* position to the bismuth and succeeded the first X–ray structure analysis of a bismuthane imide, [2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl]bis(4–methylphenyl)bismuthane *N*–(trifluoromethanesulfonyl)–imide **19b**. The imides **19** were obtained by four steps starting from triarylbismuthanes Ar_3Bi, where **a**; Ar = Ph, **b**; Ar = 4–Me–C_6H_4, **c**; Ar = 4–F–C_6H_4, **d**; Ar = 4–Cl–C_6H_4, and **e**; Ar = 4–MeO–C_6H_4, treatment of $Ar_2BiOSO_2CF_3$•$(HMPA)_2$,[13] with an excess of 2–(4,4–dimethyl–2–oxazoline–2–yl)phenylmagnesium bromide **14** gave bismuthanes **15a–d** in moderate yields. Because in the case of 4–methoxyphenyl moiety, the reaction gave a complex mixture, ligand exchange reaction on the bismuth centre of bismuthane **20e** with aryllithium **21** was carried out to obtain bismuthane **15e**. Bismuthanes **15** were less stable than Ar_3Bi and readily decomposed during column chromatography on alumina or silica gel using $CHCl_3$ as the eluent to give diarylchlorobismuthanes **16** in a good yields. Alike other halobismuthanes containing an intramolecularly coordinating group,[14] the compounds **16** were quite moisture–stable. Bismuthanes **15a–e** were converted by $PhICl_2$ to dichloride **18a–e** in good yields. When gently heated in a organic solvent, these dichlorides slowly decomposed to give chlorobismuthanes **16**. On treatment with a 2:1 molar ratio of $KOBu^t$ and $CF_3SO_2NH_2$ in THF at room temperature, dichlorides **18** gave the corresponding bismuthane imides **19** in quantitative yields, while

chlorobismuthane **16b** was simply converted to amidobismuthane **17b** (Scheme 3). In contrast to pTol$_2$BiNHSO$_2p$Tol,[5] compound **17b** was thermally stable and did not undergo disproportionation in solution. All new organobisumuth compounds **15–19** were fully characterized by ^{1}H–NMR, ^{13}C–NMR, IR and elemental analyses.



Scheme 3

Reagent and conditons: i, $Ar_2BiOSO_2CF_3 \cdot (HMPA)_2$, THF; ii, SiO_2, $CHCl_3$; iii, $CF_3SO_2NH_2$, KOBu^t, THF, r.t.; iv, $PhICl_2$, CH_2Cl_2, 0 °–r.t.; v, 40–50 °C; vi, BuLi, Et_2O; vii, $(^pAn)_2BiCl$, Et_2O, viii, OxLi, THF

a; Ar = Ph
b; Ar = 4-Me-C_6H_4
c; Ar = 4-F-C_6H_4
d; Ar = 4-Cl-C_6H_4
e; Ar = 4-MeO-C_6H_4

The imides **19** are soluble in CH_2Cl_2, $CHCl_3$ and THF, but poorly soluble in Et_2O and hexane; **19a–c** can be readily purified by recrystallization from a CH_2Cl_2–Et_2O mixture, while **19d** slowly decomposed during the recrystallization procedure. The imide **19e** could be handled easily in solution like **19a–c**, however, it was difficult to obtain crystalline solids. In marked contrast to the known bismuthane imides,[3] they did not show any sign of decomposition even when stood in a wet $CHCl_3$. In acetone, they slowly decomposed to give a mixture of products in which amidobismuthane **17** was

a major component. Compound **19a–c** provide examples of moisture–insensitive bismuthane imides, which can be handled safely under atmospheric conditions. After several months storage on a bench shelf, crystals of imides **19** were still alive.

X-Ray structure analysis of compound 19b

In order to get an insight into the structure of bismuthane imide **19b**, an X-ray crystallographic study was performed. As shown in **Fig. 1**, the bismuth atom is attached by three carbon atoms C(1), C(12) C(19) and one nitrogen atom N(1), with the C–Bi–C bond angles 112.0(5)–119.9(5)° and N(1)–Bi–C bond angles 94.2(5)–107.8(5)°. The oxazoline nitrogen atom N(2) coordinates intramolecularly to the bismuth center from an apical side with a distance of 2.69(1) Å and an N(1)–Bi–N(2) bond angle of 163.5(4). The geometry around the bismuth center can be regarded as a distorted trigonal bipyramid (TBP), although the contribution of tetrahedral (TD) structure is not negligible; the bismuth atom is located 0.49 Å above the plane which three carbon atoms C(1), C(12) and C(19) make.[15] The sum of three C–Bi–C bond angles (345.4°) lies between the predicted values of a TBP (360°) and a TD structure (328.5°). From an open C(12)–Bi–C(19) side, one of the sulfonyl oxygen atoms O(1) coordinates to the bismuth with a distance of 2.97(1) Å.[16] The intramolecular distance between the bismuth and the N(2) atoms is longer than the sum of covalent radii Bi–N (2.16 Å), but shorter than the sum of van der Waals radii Bi–N (*ca* 3.6 Å). The corresponding sums of covalent radii Bi–O and of van der Waals radii Bi–O are 2.12 Å and *ca* 3.5 Å, respectively.

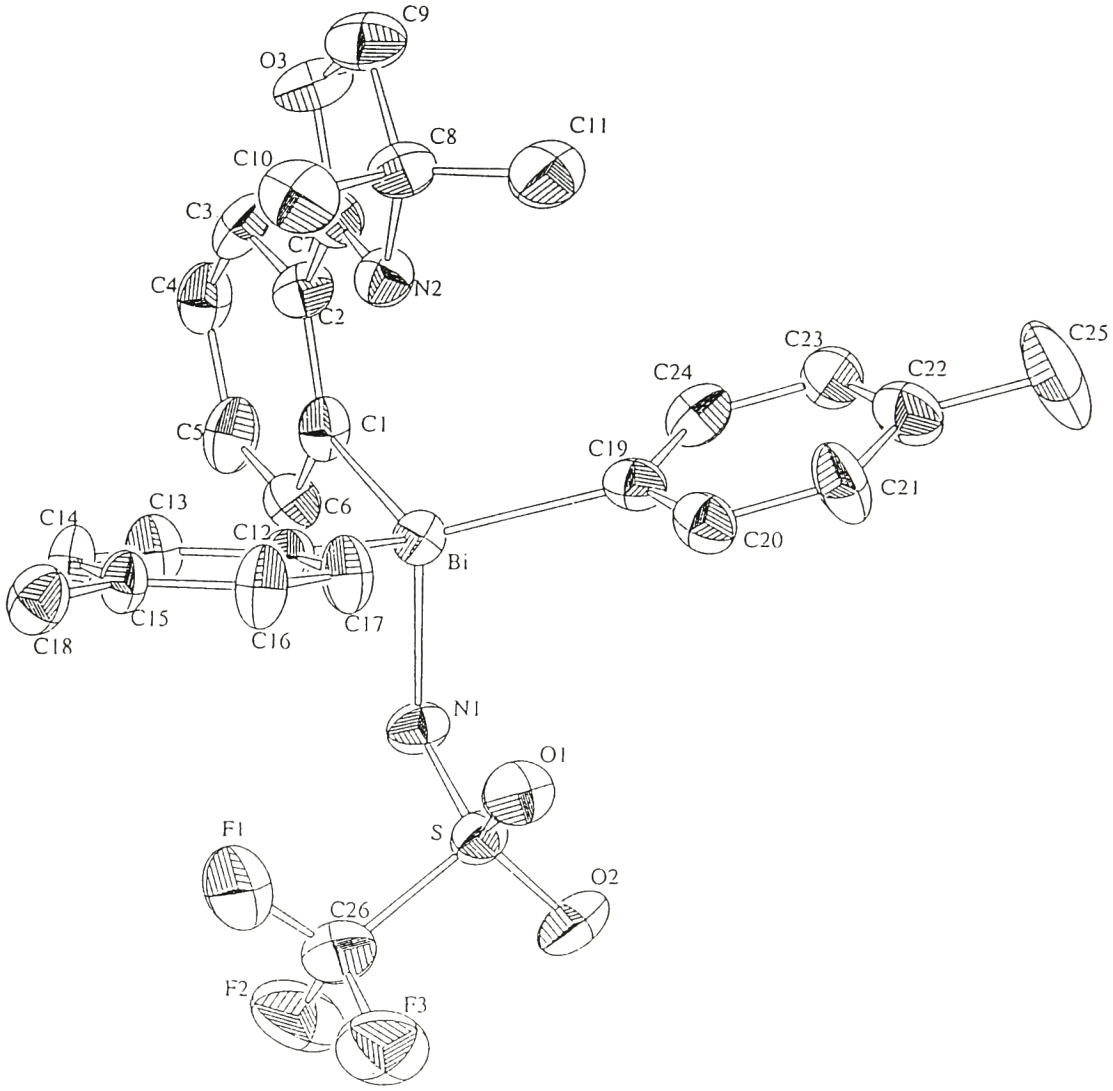


Fig. 1 ORTEP drawing of compound **19b**, with crystallographic numbering scheme. The percentage probability level of the ellipsoids in this drawing is 30%.

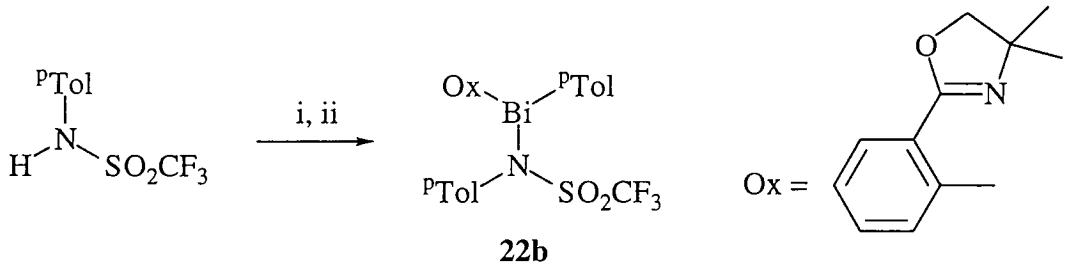
Table 3. Selected bond distances (Å) and angles [°] for imide **19b**, with estimated standard deviations in parentheses.

Bond Length		Bond Angle	
Bi–N(1)	2.13(1)	N(1)–Bi–C(1)	94.2(5)
Bi–C(1)	2.23(1)	N(1)–Bi–C(12)	107.8(5)
Bi–C(12)	2.19(1)	N(1)–Bi–C(19)	105.9(5)
Bi–C(19)	2.20(2)	C(1)–Bi–C(12)	113.4(5)
S–O(1)	1.45(1)	C(1)–Bi–C(19)	112.0(5)
S–O(2)	1.43(1)	C(12)–Bi–C(19)	119.9(5)
S–N(1)	1.53(1)	O(1)–S–O(2)	116.7(7)
Bi–N(2)	2.69(1)	O(1)–S–N(1)	114.3(7)
Bi–O(1)	2.97(1)	O(2)–S–N(1)	114.4(7)
		O(1)–S–C(26)	100.4(9)
		O(2)–S–C(26)	102.5(9)
		N(1)–S–C(26)	106.1(8)
		Bi–N(1)–S	111.0(6)
		C(1)–Bi–N(2)	69.3(5)
		C(12)–Bi–N(2)	106.0(3)
		C(19)–Bi–N(2)	82.1(5)
		N(1)–Bi–N(2)	163.5(4)

X–ray crystallography has supported that the imide **19b** possesses a similar structure both in solution and in the solid state: some characteristic features in ^{1}H–NMR spectrum of imide **19b** can be explained according to the solid structure. Highfield shift of two *gem*–methyl groups on the oxazoline ring (0.68 ppm) with respect to those of bismuthane **15b** (1.13 ppm), should be caused by the anisotropic effect of two *p*Tol groups. The *ortho* aromatic protons appeared at 7.76 (*p*Tol) and 8.97 ppm (oxazoline substituted phenyl group), respectively 0.14 and 0.99 ppm lower shifted than those of compound **15b**. This observation is indicative of the TBP structure of imide **19b**; in which the degree of deshielding effect by N(1) atom is much greater in the latter case than the former case, probably because *p*Tol group are not fixed for the direction.

The most interesting feature of compound **19b** is the Bi–N(1) bond length; the observed value 2.13(1) Å almost falls in the range of the known Bi–N single bond distance; 2.12(2)–2.28(2) Å for $(Ph_2N)_3Bi$,[17] 2.180(21)–

2.189(18) Å for $(Me_2N)_3Bi$,[18] 2.14(2)–2.214(13) Å for $[(tBu_3C_6H_2)NH]_3Bi$,[19] 2.158(4)–2.174(5) Å for a cyclic amidobismuthane,[20] and 2.101(7)–2.237(7) Å for a cubic amidobismuthane.[21] Therefore, the Bi–N(1) bond in compound **19b** can be regarded by nature as a polarized single bond, Bi^+–N^-, rather than a double bond, Bi=N. For a further detailed comparison of the Bi–N(imide) bond length and Bi–N bond in Ar_2Bi–NR, an amidobismuthane **22b** was prepared by the same procedure used for compound **17b**. In contrast to compound **17b**, amidobismuthane **22b** forms well–shaped crystals, which would be suitable for an X-ray study (Scheme 4).



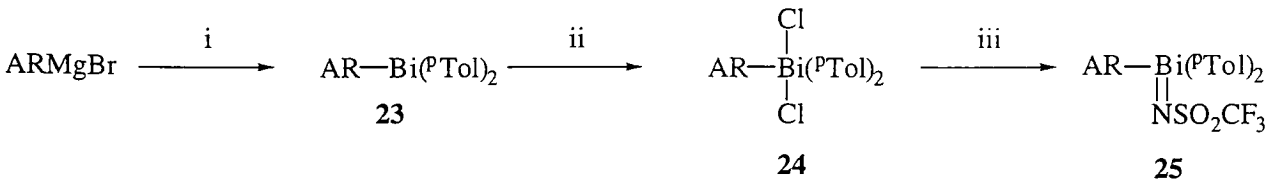
22b

Scheme 4 *Reagents and Conditions:* i, $KOBu^t$, THF, r. t.; ii, **16b**, THF, r.t.

Attempt to use {2–(*N*–Methyl–*N*–Phenylaminomethyl)phenyl} groups as a protecting group of the bismuthane imides instead of oxazoline group failed; bismuthane **23** and its dichloride **24** were prepared as well as compound **15** and **18**. Compound **24** was treated with $CF_3SO_2NH_2$ in the presence of $KOBu^t$ to give the corresponding bismuthane imide **25**, however, it decomposed into a complex mixture (Scheme 5).

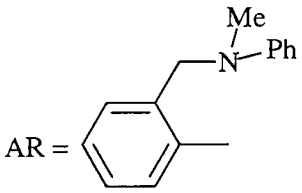
Coordination of the oxazoline nitrogen atom to the bismuth should play an important role in the stabilization of the polarized Bi–N bond, where the Bi, N(1), S and O(1) atoms as well as all ring atoms of the oxazoline [C(7)–C(9), N(2), O(3)] are nearly coplanar with a mean deviation of 0.012 Å from the

plane [C(1)–C(6)] defined by one of the benzene rings.

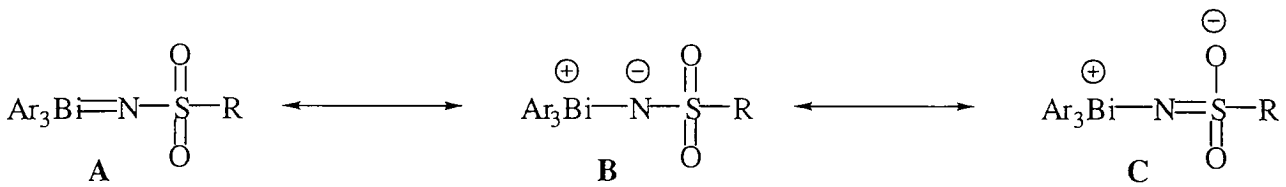


Scheme 5

Reagent and conditons: i, $(^{P}Tol)_2BiOSO_2CF_3 \cdot (HMPA)_2$, THF; ii, $PhICl_2$, CH_2Cl_2, 0 °–r.t.; iii, $CF_3SO_2NH_2$, $KOBu^t$, THF, r.t.



These observations strongly suggest that the N(2)–Bi–N(1) linkage has the nature of a so–called hypervalent bond and that a charge on the Bi–N(imide) bond would be distributed over the array of N(2)–Bi–N(1)–S–O(1) atoms in a push–pull way from the N(2) toward the O(1) end. The short N(1)–S bond distance in **7**, 1.53(1) Å, is highly suggestive of substantial multiple character, since it is 0.21 Å shorter than the sum of covalent radii of sulfur and nitrogen, 1.74 Å. In addition to this resonance stabilization between the imide and sulfonyl functions, the intramolecular coordination of the O(1) atom to the bismuth may also be effective for the stabilization of the Bi–N(imide) bond (Scheme 6). Thus, in the case of the imide **19b**, C form in Scheme 6 may be the most important structure.



Scheme 6

Our experimental result is in good accordance with a recent theoretical study on the electronic configuration of $H_3Bi{=}NH$ and $H_2Bi{-}NH_2$ at MP2/DZ–d

level, where the lengths of the Bi=N and Bi–N bonds were estimated to be 1.997 Å and 2.133 Å, respectively.[22]

Discussion on IR data

As described above, bismuthane imides are concluded to possess the polarized single bond nature (Bi^{+}–N^{-}), rather than double bond nature (Bi=N). This conclusion may be supported by the discussion on IR data of amidobismuthanes and bismuthane imides; cyclic amidobismuthane **26**, prepared as well as **17b** or **22b**, and bismuthane imide **8** exhibited strong peaks at 615 and 613 cm^{-1}, respectively. These peaks were not observed in the IR spectra of the other azabismocine derivatives, and could be considered as an adsorption due to Bi–N bonds. Similarly, the series of amidobismuthane and bismuthane imides containing oxazoline group exhibited strong peaks around 610 cm^{-1}; amidobismuthane **17b** and **22b** showed peaks at 617 and 623 cm^{-1}, respectively, while bismuthane imides **19a**, **b** and **c** showed peaks at 613, 613 and 611 cm^{-1}, respectively. These facts may suggest that Bi–N(amide) bond and Bi–N(imide) possess the similar nature.

Experimental Part

All reactions were carried out under an atmosphere of dry argon. Ether and THF were distilled under argon from sodium benzophenone ketyl before use. Triarylbismuthanes were prepared from the corresponding arylmagnesium bromides or aryllithiums with bismuth(III) chloride and recrystallized from benzene-methanol. Commercially available bismuth(III) chloride was

purified by refluxing with thionyl chloride for 2 h. Other commercially available reagents were used without further purification. Column chromatography was performed on silica gel (Wakogel, 200 mesh) or activated alumina (Wako, 300 mesh). All mps were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Coupling constant *J* values are given in Hz. IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. Elemental analyses were performed at Microanalytical Laboratory, Institute of Chemical Research, Kyoto University.

Preparation of 6–Methyl–5,6,7,12–tetrahydro–12–chloro–dibenz[c,f][1,5] azabismocine 5

To a solution of bis(2-bromobenzyl)methylamine (11.07 g, 30 mmol) in dry ether (30 cm^3), was added n-butyllithium in hexane (1.5 M, 43.3 cm^3, 65 mmol) at 0 °C, and the mixture was heated at reflux for 3.5 h under argon to give the corresponding dilithio derivative, which was added dropweise during 1.5 h at -60 °C to a solution of bismuth trichloride (10.08 g, 32 mmol) in dry ether (200 cm^3) to give a salmon pink coloured suspension. The reaction mixture was gradually warmed to -20 °C during 12 h, and then poured into cold brine (100 cm^3). The resulting suspension was filtered through a Celite bed to leave a light grey sludge, which was successively extracted with $CHCl_3$ (100 cm^3 x 3). The combined extracts were dried over Na_2SO_4, and evaporated under reduced pressure to give a light brown residue, which was

recrystallized from $CHCl_3$-EtOH (1:1) to afford *product* **1** as colourless crystals (9.69 g, 21.4 mmol, 71 %). *Compound* **5** mp 195-197 °C (lit.[9], 199-200 °C); δ_H; 2.86 (3 H, s), 4.12 (2 H, d, J_{AB} 14.3), 4.27 (2 H, d, J_{AB} 14.3), 7.30~7.60 (6 H, m) and 8.66 (2 H, d, J 7.9); ν_{max}(KBr)/cm^{-1}; 1455, 1439, 1103, 878, 822, 764, 749 and 428.

6–Methyl–12–(4–methylphenyl)–5,6,7,12–tetrahydro–dibenz[c,f][1,5] azabismocine 6

To a suspension of compound **5** (4.53 g, 10 mmol) in dry ether (20 cm^3), was added at room temperature a solution of (4-methylphenyl)magnesium bromide, prepared from 4-bromotoluene (2.46 cm^3, 20 mmol) and magnesium (0.486 g, 20 mmol) in dry ether (20 cm^3). The resulting mixture was heated at reflux for 2 days, and then poured into brine (50 cm^3). Ether was removed under reduced pressure, and the mixture was extracted with CH_2Cl_2 (50 cm^3 x 3). The combined extracts were dried (Na_2SO_4), and evaporated under reduced pressure to give a pale yellow solid, which was recrystallized from $CHCl_3$-EtOH (1:2) to afford *product* **6** (4.00 g, 7.86 mmol, 79 %) as colourless crystals. *Compound* **2** mp 157-158 °C; δ_H; 2.40 (3 H, s), 2.51 (3 H, s), 3.69 (2 H, d, J_{AB} 14.3), 3.93 (2 H, d, J_{AB} 14.3), 7.05~7.28 (8 H, m) 7.59 (2 H, d, J_{AB} 6.8) and 7.76 (2 H, d, *J* 7.7); ν_{max}(KBr)/cm^{-1}; 2793, 1435, 1358, 1051, 878, 795, 749, 480 and 438 (Found: C, 51.62; H, 4.30; N, 2.72. $C_{22}H_{22}BiN$ requires C, 51.84; H, 4.32; N, 2.75%).

12,12–dichloro–6–Methyl–12–(4–methylphenyl)–5,6,7,12–

tetrahydro–12λ^5–dibenz[c,f][1,5]azabismocine 7

Chlorination with SO_2Cl_2. To a solution of compound **6** (2.545 g, 5 mmol) in CH_2Cl_2 (30 cm^3), was added SO_2Cl_2 (0.402 cm^3, 5 mmol) at 0 °C, and the resulting yellow solution was stirred at room temperature for 45 min. The mixture was evaporated under reduced pressure to leave a yellow solid, which was chromatographed on silica gel, using CH_2Cl_2 as the eluent, to give *compound* **5** (0.706 g, 1.39 mmol, 28 %) and *product* **7** (1.093 g, 1.88 mmol, 38 %).

Chlorination with iodobenzene dichloride. To a solution of compound **6** (1.436 g, 2.82 mmol) in CH_2Cl_2 (50 cm^3), was added iodobenzene dichloride (0.795 g, 2.88 mmol) at 0 °C, and the resulting yellowish brown solution was stirred at room temperature for 20 min. The same work-up procedure gave *compound* **5** (0.236 g, 0.52 mmol, 19 %) and *product* **7** (1.214 g, 2.10 mmol, 74 %). *Compound* **7** mp 202-204 °C (decomp.); δ_H; 2.45 (3 H, s), 2.49 (3 H, s), 4.17 (2 H, d, J_{AB} 14.3), 4.75 (2 H, d, J_{AB} 14.3), 7.40~7.50 (6 H, m) 7.55 (2 H, d, J_{AB} 7.8) 7.65–7.75 (2 H, m) and 8.54 (2 H, d, J_{AB} 8.3); ν_{max}(KBr)/cm^{-1}; 1453, 1435, 1420, 1188, 1047, 1001, 804, 752, 745 and 474 (Found: C, 45,35; H, 3.73; N, 2.31. $C_{22}H_{22}BiCl_2N$ requires C, 45.50; H, 3.79; N, 2.41%).

6–Methyl–12–(4–methylphenyl)–5,6,7,12–tetrahydro–12λ^5-dibenz[c,f][1,5]–azabismocine *N*–trifluoromethanesulfonylimide 8

A mixture of trifluoromethanesulfonamide (0.074 g, 0.5 mmol) and potassium *tert*-butoxide (0.112 g, 1 mmol) was suspended in dry THF (5 cm^3), and

warmed to 50 °C for 20 min, then stirred at room temperature for more 30 min to give a white suspension, to which was added a suspension of compound **7** (0.290 g, 0.5 mmol) in the same solvent (25 cm^3). The resulting mixture was stirred at room temperature for 2.5 h to give a pale yellow suspension, which was evaporated under reduced pressure to leave a yellow oil. The residue was dried in vacuo to remove THF completely, and extracted with CH_2Cl_2 (15 cm^3 x 3). The combined extracts were evaporated under reduced pressure to leave a pale yellow glassy mass (0.349 g), which was recrystallized from acetone-C_6H_6 (1:1) to give *product* **8** as colourless crystalls (0.154 g, 0.235 mmol, 47 %). *Compound* **8** mp 177-179 °C; δ_H; 1.83 (3 H, s), 2.36 (3 H, s), 3.67 (2 H, d, J_{AB} 15.3), 3.90 (2 H, d, J_{AB} 15.3), 7.31 (2 H, d, *J* 8.1), 7.43 (2 H, d, *J* 7.2), 7.48 (2 H, d, *J* 8.1), 7.56 (2 H, t, *J* 7.2), 7.68 (2 H, t, *J* 7.4) and 8.67 (2 H, d, *J* 7.7); ν_{max}(KBr)/cm^{-1}; 1478, 1439, 1258, 1202, 1152, 1119, 994, 681, 613 and 480 (Found: C, 45,78; H, 3.70; N, 3.89. $C_{23}H_{22}BiF_3N_2O_2S \bullet 2/3C_6H_6$ requires C, 45.76; H, 3.67; N, 3.95%).

N-(2-Bromobenzyl)-*N*-methyl-2-bromoaniline 9

N-(2-Bromobenzyl)-2-bromoaniline (13.5 g, 39 mmol) was added to a mixture of formic acid (7.5 cm^3) and formalin (6.4 cm^3, 37% solution in water) and heated at reflux for 18 h. Excess acid was removed by distillation under reduced pressure, and the residue was poured into an aqueous solution of sodium hydroxide, extracted with ethyl acetate (30 cm^3 X 3), dried (Na_2SO_4) and evaporated. The orange oil was chromatographed on silica gel using hexane as eluent to give *N*-(2-bromobenzyl)-*N*-methyl-2-

bromoaniline **9** as light brown oil (9.31 g, 26.2 mmol, 67%). *Compound* **9**, oil; δ_H 2.75 (3 H, s), 4.28 (2 H, s), 6.91 (1 H, dt, *J* 7.5 and 1.8), 7.05-7.20 (2 H, m), 7.22-7.35 (2 H, m), 7.53 (1 H, dd, *J* 8.0 and 1.3) 7.58 (1 H, dd, *J* 8.0 and 1.6) and 7.73 (1 H, dd, *J* 7.7 and 1.7).

6-Hydro-11-iodo-5-methyl-[b,e][1,4]dibenzoazabismepine 10

To a solution of bismuth trichloride (9.45 g, 30 mmol) in ether (200 cm^3), was added in 3 h at -70 °C, a suspension of *N*–(2–lithiobenzyl)–*N*-methyl–2–lithioaniline, prepared from the amine **9** (10.65 g, 30 mmol) and butyllithium (40 cm^3, 64 mmol, 1.6 M solution in hexane). The resulting mixture was allowed to warm to room temperature during night, and treated with an aqueous solution of sodium iodide (6.0 g). The precipitated orange solid was filtered and extracted with hot acetone (200 cm^3 X 2). The acetone extracts were combined, and evaporated to give 6–hydro–11–iodo–5–methyl–dibenz[b,e][1,4]azabismepine **10** (10.02 g, 18.9 mmol, 63%) as light orange solid. This crude product was pure enough to use for further synthesis. The bismepine **10** was further purified by recrystallization from acetone. *Compound* **10**, mp, 284-285 °C; δ_H 3.14 (3 H, s), 4.40 (1 H, d, J_{AB} 16.0), 5.10 (1 H, d, J_{AB} 16.0), 7.30-7.35 (3 H, m), 7.50-7.60 (3 H, m), 8.89 (1 H, d, *J* 6.3) and 9.02 (1 H, d, *J* 7.8); δ_C 45.8, 64.5, 123.6, 128.0, 128.7, 129.8, 130.3, 132.1, 135.0, 143.7, 154.0, 156.6 and 165.2; ν_{max}(KBr)/cm^{-1} 1454, 1433, 960, 773, 760, 744, 723 and 436 (Found: C, 31.54; H, 2.07; N, 2.72. $C_{14}H_{13}BiIN$ requires C, 31.66; H, 2.47; N, 2.64%).

6-Hydro-5-methyl-11-(4-methylphenyl)-[b,e][1,4]dibenzoazabismepine 11

To a solution of 4-methylphenylmagnesium bromide, prepared from 4-methylbromobenzene (1.71 g, 10 mmol) and magnesium (0.243 g, 10 mmol) in THF (10 cm^3), was added a suspension of iodobismuthane **10** (3.61 g, 6.8 mmol) in THF (20 cm^3). The resulting suspension was heated at reflux for 1.5 h, poured into water, and extracted with chloroform (100 cm^3 X 3). The combined extracts were dried (Na_2SO_4) and evaporated to give yellow oily residue. H-NMR spectrum of the reaction mixture exhibited that the desired 6-hydro-5-methyl-11-(4-methylphenyl)-dibenz[b,e][1,4]azabismepine **11** was the major product as follows; δ_H 2.28 (3 H, s), 2.89 (3 H, s), 4.06 (1 H, d, J_{AB} 15.4), 4.36 (1 H, d, J_{AB} 15.4), 6.94(1 H, dt, J 7.0 and 1.6), 7.10-7.40 (9 H, m) and 7.55-7.75 (4 H, m). Attempt to purify the mixture by chromatography on alumina led to partial decomposition of the product.

11,11-dichloro-6-Hydro-5-methyl-11-(4-methylphenyl)-11λ^5-dibenz[b,e][1,4]azabismepine 12

To a solution of crude bismuthane **11** (3.0 g, ca. 6 mmol) in $CHCl_3$ (20 cm^3), was added $PhICl_2$ (1.595 g, 5.8 mmol) and the resulting solution was stirred at room temperature for 30 min to give a bright yellow solution, which was filtered through a Celite bed. The filtrate was evaporated to give a brown-yellow semisolid (4.77 g), which was chromatographed on silica gel using $CHCl_3$ as the eluent to afford crude 11,11-dichloro-6-Hydro-5-methyl-11-

(4–methylphenyl)–12λ^5–dibenz[b,e][1,4]azabismepine **12**. The crude product was recrystallized from $CHCl_3$–EtOH (1:1, 30 cm^3) to give pure dichloride **12** as bright yellow crystals (1.80 g, 47%), mp, 173–175 °C (decomp.); δ_H 2.49 (3H, s), 2.91 (3 H, s), 4.16 (1 H, d, J_{AB} 15.4), 5.18 (1 H, d, J_{AB} 15.4), 7.32 (1 H, ddd, *J*7.8, 6.4 and 2.2), 7.40-7.55 (5 H, m), 7.59 (2 H, d, J_{AB} 9.0), 7.78 (1 H, dd, *J*7.4 and 1.2), 7.80 (1H, d, *J*7.6) and 8.65 (2 H, d, J_{AB} 8.4); δ_C 21.4, 39.1, 63.0, 123.8, 127.1, 130.2, 130.5, 130.7, 131.2, 131.6, 131.9, 132.5, 135.4, 139.4, 142.4, 147.1, 150.5, 163.1 and 163.24; ν_{max}(KBr)/cm^{-1} 1580, 1466, 1443, 1190, 997, 760, 468 and 430 (Found: C, 44.27; H, 3.40; N, 2.46. $C_{21}H_{20}BiCl_2N$ requires C, 44.54; H, 3.56; N, 2.47%).

6–Hydro–5–methyl–11–(4–methylphenyl)–[b,e][1,4]dibenzoazabismepine *N*–trifluoromethanesulfonylimide 13

A mixture of trifluoromethanesulfonamide (0.074 g, 0.5 mmol) and potassium *tert*-butoxide (0.112 g, 1 mmol) was suspended in dry THF (5 cm^3), and warmed to 50 °C for 20 min, then stirred at room temperature for more 30 min to give a white suspension, to which was added compound **12** (0.283 g, 0.5 mmol) and the mixture was stirred at room temperature for 3 h and evaporated to afford light brown solid residue, which was extracted with CH_2Cl_2 (30 cm^3). The combined extracts were evaporated to give crude 6–Hydro–5–methyl–11–(4–methylphenyl)–[b,e][1,4]dibenzoazabismepine *N*–trifluoro–methanesulfonylimide **13** as brown amorphous solid. *Compound* **13**, δ_H 2.35 (3 H, s), 2.71 (3 H, s), 4.28 (1 H, d, J_{AB} 16.9), 4.45 (1 H, d, J_{AB} 16.2),

7.30-7.70 (10 H, m), 8.27 (1 H, d, *J*8.0) and 8.42 (1 H, d, *J*7.4).

Preparation of 2–(4,4–dimethyl–2–oxazoline–2–yl)phenyldiaryl–bismuthanes 15a–d

Genaral procedure. To a solution of 2–(4,4–dimethyl–2–oxazoline–2–yl)phenylmagnesium bromide **14**, prepared from the corresponding bromoarene (10 mmol) and Mg (10 mmol) in THF (20 cm^3), was added in one portion a solution of $Ar_2BiOSO_2CF_3 \bullet (HMPA)_2$ (6 mmol) in the same solvent (10 cm^3) at -20 °C under Ar. The resulting mixture was stirred at room temperature for 30 min and then poured into cold brine, and the mixture was extracted with benzene (50 cm^3 x 3). The combined extracts were dried and concentrated to one tenth of the original volume. Methanol (50 cm^3) was added to the concentrate and the mixture was stood at -15 °C to give bismuthanes **15** as colorless crystals.

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–diphenylbismuthane 15a. Yield 58%; mp 99–100 °C; δ_H 1.10 (6 H, s), 3.95 (2 H, s), 7.18–7.42 (8 H, m), 7.74 (4 H, dd, *J*7.6 and 1.5), 7.83 (1 H, dd, *J* 7.2 and 1.2) and 8.01 (1 H, dd, *J*7.5 and 1.6); δ_C 28.3, 67.7, 79.0, 126.9, 127.4, 129.5, 130.1, 130.4, 133.2, 137.5, 137.7, 139.4, 160.2 and 164.3; ν_{max}(KBr)/cm^{-1} 1653 (C=N), 1309, 1070, 1034, 777, 723, 682 and 449.

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis(4–methylphenyl)–bismuthane 15b. Yield 69%; mp 112–113 °C; δ_H 1.13 (6 H, s), 2.30 (6 H, s), 3.97 (2 H, s), 7.15 (4 H, d, J_{AB} 7.3), 7.25 (1 H, dt, *J*7.3 and 1.7), 7.38 (1 H, dt, *J*7.4 and 1.7), 7.62 (4 H, d, J_{AB} 7.8), 7.85 (1 H, dd, *J*7.2 and

1.5) and 7.98 (1 H, dd, *J* 7.5 and 1.7); δ_C 21.5, 28.4, 67.7, 79.0, 127.3, 129.4, 131.0, 133.0, 136.5, 137.8, 139.4, 159.6, 160.2 and 164.2; ν_{max}(KBr)/cm^{-1} 1644 (C=N), 1309, 1073, 1038, 795, 729, 683 and 480 (Found: C, 53.18; H, 4.60; N, 2.51. $C_{25}H_{26}BiNO$ requires C, 53.10; H, 4.63; N, 2.48%).

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis(4–fluorophenyl)–bismuthane 15c. Yield 35%; mp 115–116 °C; δ_H 1.10 (6 H, s), 3.99 (2 H, s), 7.00 (4 H, dd, J_{CH} 8.0 and J_{FH} 9.1), 7.30 (1 H, dt, *J* 7.5 and 1.4), 7.40 (1 H, dt, *J* 6.9 and 1.3), 7.65 (4 H, d, J_{CH} 7.8 and J_{FH} 6.5), 7.76 (1 H, dd, *J* 7.1 and 1.1) and 8.01 (1 H, dd, *J* 6.9 and 1.3); ν_{max}(KBr)/cm^{-1} 1647 (C=N), 1572, 1483, 1227, 1213, 1159, 1077, 820, 729 and 507 (Found: C, 48.09; H, 3.48; N, 2.42. $C_{23}H_{20}BiF_2NO$ requires C, 48.18; H, 3.52; N, 2.44%).

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis(4–chlorophenyl)–bismuthane 15d. Yield 88%; mp 156–157°C; δ_H 1.12 (6 H, s), 4.01 (2 H, s), 7.28 (4 H, dd, J_{AB} 8.1), 7.33 (1 H, dt, *J* 7.3 and 1.5), 7.43 (1 H, dt, *J* 7.4 and 1.5), 7.62 (4 H, d, J_{AB} 8.1), 7.76 (1 H, dd, *J* 7.4 and 1.4) and 8.01 (1 H, dd, *J* 7.4 and 1.4); δ_C 28.4, 67.7, 79.2, 127.8, 129.7, 130.4, 132.7, 133.2, 133.5, 139.1, 160.4, 162.5 and 164.6; ν_{max}(KBr)/cm^{-1} 1647 (C=N), 1556, 1469, 1356, 1311, 1086, 1072, 1041, 1005, 966, 802, 779, 727, 711, 684 and 486, 478. (Found: C, 45.86; H, 3.32; N, 2.33. $C_{23}H_{20}BiCl_2NO$ requires C, 45.56; H, 3.32; N, 2.31%).

Column chromatography of compound 15b

Bismuthane **15b** (ca. 3 mmol) was passed through an alumina (neutral) column using $CHCl_3$ as the eluent. chloro–2–(4,4–dimethyl–2–oxazoline–

2–yl)phenyl–(4–methylphenyl)bismuthane **16b** was obtained as colorless crystals in 80% yield. *Compound* **16b**, mp 184–186 °C: δ_H 1.13 (3 H, s), 1.43 (3 H, s), 2.24 (3 H, s), 4.24 (1 H, d, J_{AB} 8.5), 4.30 (1 H, d, J_{AB} 8.5), 7.27 (2 H, d, J_{AB} 7.4), 7.56 (1 H, dt, *J*7.5 and 1.2), 7.86 (1 H, dt, *J*7.5 and 1.3), 7.98 (1 H, dd, *J*7.2 and 1.2), 8.01 (2 H, d, J_{AB} 7.9) and 9.10 (1 H, d, *J*7.3); δ_C 21.5, 28.1, 29.2, 67.1, 80.7, 127.9, 131.1, 131.9, 132.0, 135.9, 136.8, 137.4, 137.8, 175.0, 176.0 and 179.4; ν_{max}(KBr)/cm^{-1} 1630 (C=N), 1375, 1327, 1088, 938, 793, 733 and 478 (Found: C, 42.43; H, 3.68; N, 2.70. $C_{18}H_{19}BiClNO$ requires C, 42.41; H, 3.76; N, 2.75%).

Preparation of *N*–(trifuoromethanesulfonyl)amido–2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–(4–methylphenyl)bismuthane 17b

A solution of compound **16b** (0.97 mmol) in THF (20 cm^3) was added to a solution of $CF_3SO_2NH_2$ (0.97 mmol) and *t*BuOK (0.97 mmol) in the same solvent (10 cm^3), and the resulting mixture was stirred at room temperature for 3 h. The solvent was evaporated to dryness and the residue was extracted with CH_2Cl_2 (5 cm^3 x 6). The combined extracts were concentrated to give compound **17b** as crystals in quantitative yield. *Compound* **17b**, mp 153–155 °C (decomp.); δ_H 1.01 (3 H, s), 1.42 (3 H, s), 2.27 (3 H, s), 3.96 (1 H , br s), 4.25 (1 H, d, J_{AB} 8.5), 4.30 (1 H, d, J_{AB} 8.5), 7.28 (2 H, d, J_{AB} 8.0), 7.60 (1 H, dt, *J*7.5 and 1.1), 7.86 (2 H, d, J_{AB} 7.9), 7.89 (1 H, dt, *J*7.5 and 1.4), 8.03 (1 H, dd, *J*7.7 and 1.4) and 8.66 (1 H, dd, *J*7.2 and 1,0); δ_C 21.5, 28.0, 29.0, 67.1, 81.0, 117.1, 123.5, 128.3, 131.7, 132.2, 132.4, 136.1,

136.8, 138.5, 172.6, 176.4 and 181.4; ν_{max}(KBr)/cm^{-1} 3279 (NH), 1632 (C=N), 1372 (SO_2), 1310, 1215, 1180 (SO_2), 1130, 1086, 976, 953, 729 and 617 (Found: C, 36.02; H, 3.19; N, 4.35. $C_{19}H_{20}BiF_3N_2O_3S$ requires C, 36.67; H, 3.24; N, 4.50%).

Preparation of 2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–diarylbismuth dichloride 18

General procedure for Compound 18a–d. A solution of bismuthane **15** (2 mmol) in CH_2Cl_2 (10 cm^3) was added to a suspension of $PhICl_2$ (2 mmol) in the same solvent (10 cm^3) at 5 °C. The resulting mixture was stirred at this temperature for 30 min and then concentrated under reduced pressure to one fifth of the original volume. Dilution of the concentrate with ethanol (30 cm^3) gave compound **18** as yellow crystals.

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–diphenylbismuth dichloride 18a. Yield 79%; mp 172–174°C (decomp.); δ_H 0.94 (6 H, s), 4.17 (2 H, s), 7.45–7.70 (8 H, m), 7.77 (1 H, dt, *J*7.7 and 1.2), 8.09 (1 H, dd, J 7.4 and 1.5) and 8.7 (4 H, br s); ν_{max}(KBr)/cm^{-1} 1649 (C=N), 1466, 1434, 1364, 1320, 1086, 984, 957, 739, 731, 677 and 448.

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis–(4–methylphenyl)–bismuth dichloride 18b. Yield 80%; Mp 187–189 °C (decomp.); δ_H 0.96 (6 H, s), 2.40 (6 H, s), 4.15 (2 H, s), 7.43 (4 H, d, J_{AB} 7.7), 7.53 (1 H, dt, *J*7.4 and 1.2), 7.66 (1 H, dt, *J*7.8 and 1.6), 7.79 (1 H, dd, *J*7.8 and 1.1), 8.07 (1 H, dd, *J*7.4 and 1.6) and 8.5 (4 H, br s); δ_C 21.3, 27.6, 67.9, 81.3, 124.6, 128.9, 129.8, 130.4, 131.8, 134.7, 136.0(broad), 140.9,

151.8(broad), 162.2 and 167.7; ν_{max}(KBr)/cm^{-1} 1649 (C=N), 1362, 1320, 1181, 1086, 1005, 992, 953, 808, 725 and 475 (Found: C, 46.89; H, 4.02; N, 2.13. $C_{25}H_{26}BiCl_2NO$ requires C, 45.84; H, 4.27; N, 2.13%).

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis–(4–fluorophenyl)–bismuth dichloride 18c. Yield 74%; Mp 186–188 °C (decomp.); δ_H 0.97 (6 H, s), 4.19 (2 H, s), 7.32 (4 H, t, *J* 8.7), 7.56 (1 H, ddd, *J* 7.5, XX), 7.66–7.75 (2 H, m), 8.09 (1 H, d, *J* 8.0) and 8.6 (4 H, br d); ν_{max}(KBr)/cm^{-1} 1649 (C=N), 1572, 1478, 1366, 1321, 1227, 1159, 1086, 1005, 959, 830, 820, 727 and 504.

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis–(4–chlorophenyl)–bismuth dichloride 18d. Yield 71%; Mp 175–177 °C (decomp.); δ_H 0.98 (6 H, s), 4.21 (2 H, s), 7.53–7.75 (3 H, m), 7.61 (4 H,d, J_{AB}8.7), 8.10 (1 H, dd, *J* 7.4 and 1.4) and 8.6 (4 H, br d); ν_{max}(KBr)/cm^{-1} 1647 (C=N), 1466, 1361, 1319, 1086, 1001, 989, 819, 725 and 480 (Found: C, 40,63; H, 2.92; N, 2.05. $C_{23}H_{20}BiCl_4NO$ requires C, 40.79; H, 2.98; N, 2.07%).

Preparation of 2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis(4–methoxyphenyl)bismuth dichloride 18e

2–(*tert*–Butylsulfonyl)phenyl–bis(4–methoxyphenyl)bismuthanes 20e. To a cooled (-60 °C) suspension of bis(4–methoxyphenyl)bismuth chloride, prepared from tris–(4–methoxyphenyl)bismuthane (2.12 g, 4 mmol) and bismuth(III) chloride (0.63 g, 2 mmol) in dry Et_2O (35 cm^3), was added a suspension of lithiated *tert*–butyl phenylsulfone, generated from *tert*–butyl phenylsulfone (1.188 g, 6 mmol)

and butyllithium (1.59 M, 3.89 cm^3, 6 mmol) in dry Et_2O (15 cm^3) at -60 °C. The resulting mixture was allowed to warm to room temperature during 2 h, and stirred at the same temperature for additional 3 h, and then poured into cold brine (100 cm^3). The mixture was extracted with $CHCl_3$ (3 X 50 cm^3) and the combined extracts was dried (Na_2SO_4), and concentrated under reduced pressure to leave a pale yellow solid. The solid residue was recrystallized from $CHCl_3$–EtOH (1:1, 30 cm^3) to give 2–(*tert*–Butylsulfonyl)phenyl–bis(4–methoxyphenyl)bismuthanes **20e** (2.89 g, 78%), mp 173–174 °C; δ_H 1.39 (9 H, s), 3.78 (6 H, s), 6.94 (4 H, d, J_{AB} 8.6), 7.43 (1 H, dt, *J* 7.2 and 1.5), 7.52 (1 H, dt, *J* 7.6 and 1.5), 7.58 (4 H, d, J_{AB} 8.5), 8.03 (1 H, dd, *J* 7.3 and 1.7) and 8.06 (1 H, dd, *J* 7.3 and 1.3); δ_C 24.0, 54.9, 60.5, 116.5, 127.6, 132.5, 135.4, 138.8, 139.5, 140.7, 155.1, 158.2 and 159.1; ν_{max}(KBr)/cm^{-1} 1578, 1489, 1458, 1283, 1242, 1175, 812, 731, 642 and 573 (Found: C, 46.19; H, 4.37. $C_{24}H_{27}BiSO_4$ requires C, 46.46; H, 4.39%).

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis(4–methoxyphenyl)–bismuth dichloride 18e. To a cooled (-78 °C) solution of bismuthane **20e** (0.620 g, 1 mmol) in THF (20 cm^3), was added a suspension of 2–(4,4–dimethyl–2–oxazoline–2–yl)phenyllithium **21**, prepared from 2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl iodide (0.602 g, 2 mmol) and butyllithium (1.54 M, 1.3 cm^3, 2 mmol) in THF (10 cm^3). The resulting bright yellow suspension was allowed to warm to room temperature during 3 h, and poured into a cold brine (50 cm^3). The mixture was extracted with $CHCl_3$ (50 cm^3 X 3) and the combined extracts were evaporated to give a brown oily residue, which was treated with $PhICl_2$ (0.275

g, 1.0 mmol) in CH_2Cl_2 (10 cm^3)at room temperature. The mixture was concentrated after 10 min, and the residue was chromatographed on silica gel using CH_2Cl_2 as the eluent to give dichloride **18e** as pale yellow crystals (0.360 g, 54%), mp 164–166 °C, δ_H 0.98 (6 H, s), 4.16 (2 H, s), 7.12 (4 H, d, J_{AB} 9.0), 7.54 (1 H, dt, *J* 7.3 and 1.2), 7.67 (1 H, dt, *J* 7.6 and 1.6), 7.78 (1 H, d, *J* 7.7), 8.07 (1 H, dd, *J* 7.4 and 1.5) and 8.5 (4 H, br d); ν_{max}(KBr)/cm^{-1} 1651 (C=N), 1570, 1483, 1362, 1294, 1250, 1175, 1082, 1026, 990, 961, 831, 822, 774, 727 and 507 (Found: C, 44.85; H, 3.83; N, 2.05. $C_{25}H_{26}BiCl_2NO_3$ requires C, 44.93; H, 3.92; N, 2.10%).

Preparation of 2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–diarylbismuth *N*–(trifluoromethanesulfonyl)imides 19

General procedure. The dichloride **18** (0.5 mmol) suspended in THF (15 cm^3) was added to a suspension of $CF_3SO_2NH_2$ (0.5 mmol) and *t*BuOK (1 mmol) in the same solvent (10 cm^3), and the resulting mixture was stirred at room temperature for 1.5 h. The solvent was evaporated to dryness and the residue was extracted with CH_2Cl_2 (10 cm^3 x 4). The combined extracts were evaporated to one tenth of the original volume, and Et_2O (10 cm^3) was added and the mixture was stood at -15 °C to deposit the imide **19**.

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–diphenylbismuth *N*–(trifluoromethanesulfonyl)imide 19a. Yield 65%, mp 178–180 °C; δ_H 0.63 (6 H, s), 4.10 (2 H, s), 7.40–7.65 (6 H, m), 7.77 (1 H, t, *J* 7.5), 7.88 (4 h, d, *J* 7.2), 7.97 (1 H, t, *J* 7.7), 8.14 (1 H, d, *J* 7.3) and 8.97 (1 H, d, *J* 7.7); δ_C 27.0,

67.8, 81.1, 118.4, 124.9, 130.0, 130.1, 131.4, 132.2, 134.0, 135.4, 137.7, 144.4, 151.7 and 164.2; ν_{max}(KBr)/cm^{-1} 1642 (C=N), 1439, 1372 (SO_2), 1252, 1170, 1150 (SO_2), 980, 733, 683, 613 and 448.

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis(4–methylphenyl)–bismuth *N*–(trifluoromethanesulfonyl)imide 19b. Yield 90%, mp 188–190 °C (decomp.); δ_H 0.68 (6 H, s), 2.38 (6 H, s), 4.10 (2 H, s), 7.36 (4 H, d, J_{AB} 8.3), 7.76 (4 H, d, J_{AB} 8.1), 7.7 (1 H, dt, J value could not determined), 7.96 (1 H, dt, *J*7.7 and 1.3), 8.12 (1 H, dd, *J*7.6 and 1.5) and 8.97 (1 H, d, *J* 7.8); δ_C 21.4, 27.2, 67.8, 81.1, 118.5, 125.0, 130.0, 131.8, 132.0, 133.8, 135.3, 137.6, 141.8, 144.6, 148.2 and 164.1; ν_{max}(KBr)/cm^{-1} 1642 (C=N), 1370 (SO_2), 1254, 1204, 1159 (SO_2), 1113, 1090, 988, 793, 613 and 478 (Found: C, 43.32; H, 3.62; N, 3.85. $C_{26}H_{26}BiF_3N_2O_3S$•0.5H_2O requires C, 43.28; H, 3.77; N, 3.88%).

2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–bis(4–fluorophenyl)–bismuth *N*–(trifluoromethanesulfonyl)imide 19c. Yield 80%, mp 191–193 °C; ν_{max}(KBr)/cm^{-1} 1644 (C=N), 1576, 1483, 1368 (SO_2), 1240, 1225, 1202, 1175, 1113, 986, 828, 791, 644, 611 and 505.

Preparation of *N*–(4–methylphenyl)–*N*–(trifuoromethanesulfonyl)–amido–2–(4,4–dimethyl–2–oxazoline–2–yl)phenyl–(4–methylphenyl)bismuthane 22b

A solution of compound **16b** (0.5 mmol) in THF (10 cm^3) was added to a solution of CF_3SO_2NH(*p*Tol) (0.5 mmol) and *t*BuOK (0.5 mmol) in the same solvent (10 cm^3), and the resulting mixture was stirred at room temperature

for 2 h. The solvent was evaporated to dryness and the residue was extracted with CH_2Cl_2 (5 cm^3 x 6). The combined extracts were concentrated to give compound **22b** as crystals. Recrystallization from CH_2Cl_2–hexane gave colourless crystals of *compound* **22b**, mp 165–167 °C (decomp.); δ_H 0,90 (3 H, s), 1.40 (3 H, s), 2.13 (3 H, s), 2.16 (3 H, s), 4.12 (1 H , d, J_{AB} 8.5), 4.21 (1 H, d, J_{AB} 8.5), 6.60 (2 H, d, J_{AB} 8.6), 6.66 (2 H, d, J_{AB} 8.7), 7.02 (2 H, d, J_{AB} 7.7), 7.50 (2 H, d, J_{AB} 7.7), 7.58 (1 H, t, *J*7.5), 7.96 (1 H, t, *J*7.1) and 7.98 (1 H, d, *J*7.5) and 8.80 (1 H, d, *J*7.3); ν_{max}(KBr)/cm^{-1} 1634 (C=N), 1507, 1380 (SO_2), 1320, 1252, 1210, 1160, 1132, 1090, 986, 943, 845, 795, 729, 706, 623, 590, 513 and 478 (Found: C, 43.88; H, 3.63; N, 3.91. $C_{26}H_{26}BiF_3N_2O_3S$ requires C, 43.83; H, 3.68; N, 3.93%).

Preparation of {2–(*N*–methyl–*N*–phenylaminomethyl)phenyl}–bis–(4–methylphenyl)bismuthane 23

A solution of 2-(*N*-methyl-*N*-phenylaminomethyl)phenyllithium prepared from 2-bromo–(*N*–methyl–*N*–phenylaminomethyl)benzene (0.905 g, 3.28 mmol) and butyllithium (2.2 cm^3, 3.5 mmol, 1.6 M in hexane) in Et_2O (10 cm^3) was added in 10 min at -70 °C to a suspension of chlorobis–(4–metylphenyl)bismuthane, prepared from tris–(4–metylphenyl)bismuthane (1.054 g, 2.187 mmol) and bismuth(III) chloride (0.344 g, 1.093 mmol) in the same solvent (10 cm^3). The reaction mixture was allowed to warm to room temperature during 10 h, and the solvent was evaporated under reduced pressure. The residue was treated with water and extracted with $CHCl_3$ (30 cm^3 X 3), and the extracts were combined, dried (Na_2SO_4), and filtered. The

filtrate was evaporated under reduced pressure. Chromatography on alumina gel with hexane as the eluent gave tris–(4–metylphenyl)bismuthane (0.200 g, 19%) and {2–(*N*–methyl–*N*–phenylaminomethyl)–phenyl}–bis–(4–methylphenyl)bismuthane **23** (1.130 g, 1.92 mmol, 59%) as colourless crystals, mp 90–91 °C; δ_H 2.29 (6 H, s), 2.57 (3 H, s), 4.35 (2 H, s), 6.69–6.82 (3 H, m), 7.14 (4 H, d, J_{AB} 7.7), 7.13–7.37 (5 H, m), 7.54 (4 H, d, J_{AB} 7.7) and 7.79 (1 H, d, *J*7.1); δ_C 21.5, 39.0, 60.6, 114.9, 118.4, 127.8, 128.9, 129.9, 131.1, 131.2, 137.0, 137.7, 139.5, 144.1, 150.2, 152.2 and 156.4; ν_{max}(KBr)/cm^{-1} 1601, 1502, 1319, 1257, 1186, 1032, 1012, 792, 758, 692 and 478 (Found: C, 57.16; H, 4.73; N, 2.26. $C_{28}H_{28}BiN$ requires C, 57.24; H, 4.80; N, 2.38%).

{2–(*N*–methyl–*N*–phenylaminomethyl)phenyl}–bis–(4–methylphenyl)–bismuth dichloride 24

The bismuthane **23** (4.70 g, 8 mmol) was treated with $PhICl_2$ (2.20 g, 8 mmol) in CH_2Cl_2 (30 cm^3) at 0–5 °C for 1 h. The mixture was evaporated to give a deep orange oily residue, which was chromatographed on silica gel using hexane–EtOAc (6:1–2:1) to obtain a crude product. Recrystallization from CH_2Cl_2–EtOH gave the *product* **24** as orange crystals, mp 163–165 °C; δ_H 2.34 (6 H, s), 2.72 (3 H, s), 4.69 (2 H, s), 6.72–6.85 (3 H, m), 7.01 (2 H, t, *J*7.8), 7.27 (4 H, d, J_{AB} 8.1), 7.42–7.52 (3 H, m), 7.82–7.89 (1 H, m) and 8.27 (4 H, d, J_{AB}8.2); ν_{max}(KBr)/cm^{-1} 1579, 1505, 1235, 1179, 1092, 994, 799, 752, 685, 477 and 467 (Found: C, 50.52; H, 4.25; N, 2.01. $C_{28}H_{28}BiN$ requires C, 51.08; H, 4.29; N, 2.13%).

6–Methyl–5,6,7,12–tetrahydro–12–(trifluoromethanesulfonyl)amido–dibenz[c,f][1,5] azabismocine 26

A solution of compound **5** (0.453 g, 1.0 mmol) in THF (20 cm^3) was added to a solution of $CF_3SO_2NH_2$ (0.149 g, 1.0 mmol) and *t*BuOK (0.112 g, 1.0 mmol) in the same solvent (5 cm^3), and the resulting mixture was stirred at room temperature for 2 h. The solvent was evaporated to dryness and the residue was extracted with $CHCl_3$ (15 cm^3 x 3). The combined extracts were concentrated to afford a white solid, which was recrystallized from CHCl3–Et2O to give compound **26** as colourless crystals (0.378 g, 67%). *Compound* **26**, mp 190–192 °C; δ_H 2.82 (3 H, s), 4.11 (2 H, d, J_{AB} 14.6), 4.28 (2 H, d, J_{AB} 14.6), 7.37 (2 H, dt, *J* 7.4 and 1.2), 7.48 (1 H, t, *J* 7.4), 7.55 (2 H, dt, *J* 7.4 and 1.4) and 8.25 (2 H, d, *J* 7.4); ν_{max}(KBr)/cm^{-1} 3276 (NH), 1439, 1323 (SO_2), 1213, 1179 (SO_2), 968, 750 and 615 (Found: C 33.90; H 2.75; N 4.96. $C_{16}H_{16}BiF_3N_2SO_2$ requires C, 33.93; H, 2.85; N, 4.95%).

X–Ray crystallography of compound 19b

A crystal of dimensions 0.32 x 0.10 x 0.10 mm, grown from mixture of CH_2Cl_2–Et_2O (1:1) at room temperature was used for X–ray crystallography.

Crystal data. $C_{26}H_{26}BiF_3N_2O_3S$. Monoclinic. Space group C2/c (No 15), a = 25.556(3), b = 15.137(3), c = 17.563(2) Å, β = 125.263(7)°, V = 5547(1) $Å^3$, Z = 8, D_C = 1.706 gcm^{-3}, μ(Mo-Kα, λ = 0.71069 Å) = 64.7 cm^{-1}.

Data collection and processing. Intensity data were collected on a Rigaku AFC7S diffractometer using graphite–monochromated Mo-Kα radiation at 25±1 °C using ω-2θ scan technique to a maximum 2θ value of

55.0°. Of the 6767 reflections which were collected for Lorentz and polarization effect, 6619 were unique (R_{int} = 0.066).

Structure analysis and refinement. The structure solution and refinement was carried out with Patterson Method (DIRDIF92 PATTY) and Full–matrix least–squares, the non–hydrogen atoms were refined anisotropically. No. of observations was 2652 reflections with $I > 3.00\sigma(I)$, 325 variables, no decay correction was applied. R = 0.047, R_w = 0.060. Hydrogen atoms were included but not refined. All calclation were performed using the TEXSAN[24] crystallographic software package of the Molecular Structure Corporation. The ORTEP[25] program was used to obtain the drawing in Fig. 1. Further details of the crystal structure investigation may be obtained from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ (UK), on quoting the depository number 100431.

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